ASSESSMENT OF ALTERNATIVE OCEAN SLUDGE DISPOSAL PRACTICES

Interim Report to

LOS ANGELES/ORANGE COUNTY METROPOLITAN AREA
REGIONAL WASTEWATER SOLIDS MANAGEMENT PROGRAM

by

George Jackson

in collaboration with

James J. Morgan
Robert C. Y. Koh
Norman H. Brooks

Environmental Quality Laboratory
California Institute of Technology
Pasadena, California 91125

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PREFACE

PRELIMINARY CONCLUSIONS FOR CONSIDERATION BY LA/OMA PROJECT

by

Norman H. Brooks

This study is part of EQL's ongoing research on the assessment of various practices for ocean disposal of digested sewage sludge, with particular reference to the Southern California Bight. Two reports have been issued previously.

This report presents work in progress since early 1977, with support of the Rockefeller Foundation and three local sewage agencies (City of Los Angeles, Sanitation Districts of Los Angeles County, and Sanitation Districts of Orange County). The latter contract[2] covers LA/OMA sub-element 5.2[3] except for limited field work being done under a separate contract by the Southern California Coastal Water Research Project.

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[1] Faisst, W. K., Digested Sewage Sludge: Characterization of a Residual and Modeling for its Disposal in the Ocean off Southern California, Environmental Quality Laboratory Report No. 13, California Institute of Technology, Pasadena, California, June 1976.

Isaacson, M. S. and N. H. Brooks, eds., Report on Mini-Conference on Sludge Disposal Alternatives in the Ocean off Southern California, 8 September 1976, Environmental Quality Laboratory Memorandum No. 19, California Institute of Technology, Pasadena, California, December 1976.

[2] See Appendix 3 for copy of scope of work in EQL's contract.

[3] Regional Wastewater Solids Management Program, Los Angeles/Orange County Metropolitan Area (Whittier, California), Phase I Report, August 1976, pp. VII-46,47.

The general framework of engineering alternatives for regional ocean sludge disposal is well described in a report by Raksit[4], and will not be repeated here. The various ocean disposal alternatives are less costly than all land-disposal and incineration/pyrolysis systems studied.[4,5] Even though ocean sludge disposal is currently contrary to both state and federal regulations, it is hoped that this study will advance our scientific and engineering knowledge of the effects of sludge discharge in deep water, in case the regulatory policy is reexamined in the future.

Much of the work under the contract is still in progress, as it has been in effect only for four months. The quantitative predictions given are all to be considered preliminary; so far our attention has been mostly on methodology. In the final report all sludge input data (particularly heavy metals) will be updated, and we will also have available some deep ocean current data, some chemical profiles, and biotic surveys from SCCWRP.

Consequently it is impossible to make firm conclusions at this time; nonetheless, because of the needs of the LA/OMA project, we offer the following preliminary conclusions. It is essential to

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[4]Raksit, S. K., "Initial Analysis of Ocean Disposal as a Sludge Management Candidate System," Report, c/o LA/OMA Project, P.O. Box 4998, Whittier, California 90607.

[5]CH_2M Hill, Inc., "Initial Analysis of Candidate Systems and Preliminary Site Identification," Report to LA/OMA, April 1977.

realize that all these are subject to change, but taken as a whole they should provide some insights into our general thinking and some early guidance for further narrowing the range of options deserving engineering study.

PRELIMINARY CONCLUSIONS

1. Classification of offshore basin waters. In discussing the possible alternatives and their impacts it is useful to categorize the offshore basin waters in three parts:

a. Lower basin water--the body of water which is within topographic depressions, and below the lowest of the sills surrounding a basin.

b. Upper basin water--those waters which are in layers that are partially enclosed in basins, perhaps with an opening at one end but contained along the sides and at the opposite end by submarine mountain ranges and sills.

c. Upper shelf water--the water mass which is generally above the submarine mountain ranges so that its lateral flow and circulation are relatively unimpeded by the basin topography.

For the Santa Monica-San Pedro Basin, the principal focus of our study, the approximate depth ranges are as follows:

a. Lower basin waters: below 740 meters

b. Upper basin waters: between 300 meters and 740 meters

c. Upper shelf waters: above 300 meters

2. Physical and chemical characteristics of basin waters. The salient characteristics of these three bodies of water for modeling the disposal and ultimate fate of sludge are as follows:

a. Lower basin water: D.O. in water column very low (less than 0.3 mg/ℓ); little density stratification (uniform temperature and salinity); principal water exchange caused by dense water inflows over the end sills, which flow down into the basin to lower or bottom depths, thereby causing gradual upward displacement; sediments may be aerobic in the top few centimeters but below that generally anaerobic.

b. Upper basin water: some slight density stratification due to a modest temperature gradient; dissolved oxygen still very low but gradually increasing toward the top of the layer due to downward diffusion. Water exchange mechanism is not clear yet but probably greater horizontal exchange than for the lower basin water.

c. Upper shelf water: the dissolved oxygen now rapidly approaches saturation with decreasing depth; temperature increases more rapidly, horizontal currents believed to be much stronger than in basin waters, with significant exchange with the open ocean.

3. Effects of settling velocity of sludge particles and sludge density on fate of particles. There is still considerable uncertainty about the settling velocity of sludge particles, because of coagulation and/or flocculation in the ocean, which is practically impossible to reproduce in the laboratory. Furthermore, the inclusion of more secondary sludge in the total mass should greatly increase the number of fine particles in a way not yet fully predictable.

The method of sludge discharge in the ocean affects the relevance and importance of particle settling in the following sense: if the

sludge is thin (the water fraction being fresh water), then upon discharge from an outfall a buoyant plume will develop which carries the particles and fluid up several tens or a hundred meters in the water column to a place of neutral density. Thereupon, after the initial buoyancy effect is lost, the particles will gradually start "raining" out over a large area. Larger particles settle faster and reach the bottom nearer the outfall; smaller particles travel greater distances before reaching the bottom, especially because of the gradual upwelling. Similarly, thin sludge discharged from a barge will first spread near the surface (presuming near-surface discharge) before the particles fall out.

On the other hand, if sludge is thickened to an overall density greater than sea water before discharge then there will be the possibility of a sinking plume for a barge discharge. In this case the fluid and particles will sink together at a rate far more rapid than the individual particle settling velocities. The total mass may sink as a blob to the bottom (or most of the way). If the point of discharge is moved close to the bottom by a hanging flexible pipe then the sludge mass may simply spread out slowly as a fluid density current building up a significant sludge deposit over a small area. This method avoids particles sinking one by one through the water column, exchanging with the water as they fall.

4. Basic strategies: dispersal vs. containment. The "dispersal" alternative is based on the concept that, if the sludge particles are

widely enough dispersed and settle over a large enough area of the ocean, the environmental impact will be limited to acceptably small levels. On the other hand, "containment" strategy follows the concept that, if the sludge solids can be deposited in a relatively small area (a square kilometer or so), then the environmental effects will be of minor consequence for the overall ecosystem of the basin in which this containment area is located, although more intensive at that particular dumping area.

Strategies which fall in between these opposites, i.e. limited dispersal or "leaky" containment, are likely to be unsatisfactory because they may lead to significant environmental impacts over moderately large areas.

5. Uncertainties of Physical Modelling. The disposal of sludge particles by dispersal is difficult to predict or model because of the relatively close balance in the basins between the gradual upward flow and the downward settling. Horizontal motions are also largely unknown at this time. We do expect to receive some current data from SCCRWP in the near future. We are developing our mathematical models with a range of parameters in order to test the sensitivity of the conclusions to the uncertainty of the basic information.

6. Comments on dispersal options. Thin sludge discharged through a deep water outfall into the lower basin waters could be characterized better as a dispersal strategy than as one of containment. (In fact, this is an example of an in-between strategy which is neither a good

dispersal nor a good containment). We would predict that the particles might become widely dispersed throughout a deep basin.

The rate of sedimentation on the bottom will be about half the natural sedimentation rate but the process may leave undesirable effects on the water column above. The dissolved oxygen in some parts or perhaps all of the basin might be pushed down to zero because the natural oxygen supply processes of downward diffusion or bottom water influx may not match the additional BOD of the injected particles. The release of heavy metals may be significant because the particles will be widely dispersed and there may be just enough oxygen to allow significant dissolution.

If a dispersal strategy is to be followed, it may be desirable to discharge sludge into the lower part of the upper shelf water (250-300 meters deep) where we would expect to find much larger horizontal circulation dispersing the particles, and their water column effects, over a much wider area than a single basin. The fact that there is much more oxygen in the upper shelf water probably is an indicator of the greater transfer of the surface water with the open ocean far away from both natural and man-made BOD inputs.

7. Comments on containment options. There may be significant advantages to following a containment strategy rather than a dispersal strategy because the sludge particles would be given very limited opportunity to react with the surrounding seawater, depleting oxygen and releasing metal ions. For an effective containment strategy, the

sludge should be thickened to make it significantly denser than seawater, whereupon it would be probably too thick for pumping through a pipeline. Therefore, barge disposal would be called for; one option for discharge would be to release it rapidly from a bottom dump to make as large a mass as possible so that it will sink as a continuous blob all the way to the bottom (this can be simulated later). Alternatively a hanging pipe could be developed which would allow discharge to be made close to the bottom as in a tremie concrete operation. This would give the most assurance of actually laying the material on the bottom without mixing with the surroundings, but on the other hand presents some engineering difficulties which need to be resolved.

For the containment strategy, which is essentially like making a "landfill" under water, the best sites would be in some of the deepest places in one of the basins, where we would expect to have the least current and the greatest isolation.

* * *

Because of the shortness of time we are not able to present all of the supporting evidence for these preliminary conclusions in this report, nor do we guarantee that they will be in the final conclusions. Nevertheless we have taken the unusual step of setting down these preliminary tentative conclusions to assist the LA/OMA project staff and to encourage questions and discussion which will help us in the remainder of this EQL study.

N.H.B.

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I. INTRODUCTION

Disposal of human wastes has always involved an impact on the environment. Treatment of digested sewage waste for ten million people in the Los Angeles/Orange County area yields a sludge that can be disposed of on land, in the ocean, or in the atmosphere. It is necessary to explore the environmental costs associated with each disposal possibility.

Availability of deep water close to shore in Southern California has stimulated oceanic discharge of sewage effluent and sludge. Discharge systems adequately meet the classical design criteria of maintaining aquatic oxygen concentrations and of meeting bathing water standards, but have had documented effects on marine benthic ecosystems. While the significance of ecological changes is not understood there are plans being made to change sludge disposal practices. Federal policy is to stress land disposal. Higher costs involved in land disposal make comparisons with ocean disposal desirable. One option which might have minimal environmental impact is disposal in deep oceanic basins off Los Angeles. Present low oxygen concentrations in basin waters have made them relatively devoid of animal life. Discharge of sewage sludge into such locations may have minimal impact on such ecosystems. We propose to assess the likely consequences of such a discharge.

Although oceanic disposal of organic wastes has had an impact on marine ecosystems, the magnitude of effects, mechanistic causes, and their significance are either unknown or controversial. Uncertainty at all levels of environmental study, be it physical, chemical, or biological, makes it difficult to understand or predict environmental

effects of marine waste disposal. Three important ways that sewage sludge can affect organisms are: by decreasing oxygen content in the water; by increasing sulfide concentrations in the sediments and in the waters; by changing trace metal concentrations. We can assess the impact of a proposed sludge disposal scheme by using our knowledge of the chemical process that influence oxygen, sulfide and trace metal concentrations.

San Pedro and Santa Monica Basins are the ones nearest to Los Angeles. Properties of basin waters are controlled in part by communication with open ocean waters at the San Pedro Basin sill depth of 737 m. The interconnected basins have an area of 2460 km^2 and a volume of 290 km^3 below that sill depth. Oxygen concentrations in the basins are about 0.2 ml/l (surface concentrations are about 7 ml/l). Low basin oxygen concentrations result from the presence of the oxygen minimum in the oceanic water at the sill depth as well as organic matter decay in the basins. Benthic surveys have found 81 species of invertebrates with an average density of 12-30 organisms/m^2.

Sludge disposal into San Pedro-Santa Monica Basin would have several predictable effects. Most importantly, the oxygen concentration of an already low-oxygen environment would be further lowered and the small number of organisms present would decrease. The extent of the oxygen decrease would depend on mixing rates between basin and overlying waters, on rates of sedimentation and on rates of oxygen utilization. By using mixing rates measured in other basins, oxygen utilization rates, and sedimentation models we are predicting oxygen changes. Trace metal behavior is also being predicted.

Biological assessment will be made by comparing predicted oxygen, sulfide and trace metal concentrations with data available for biological effects under those conditions. This will yield an assessment of ecological effects over the range of predicted chemical distributions.

Our study thus far has centered on collecting chemical information on sludge degradation (Appendix 1), and on establishing rates of circulation, mixing, and oxygen consumption in the nearshore basins (Appendix 2). Our modelling studies are still in progress and only a simple model of the lower basin is presented here.

We have not yet received the results of field data being collected by SCCWRP. Their current measurements will help us establish our circulation models; their biological sampling will allow us to assess the biological impact of conditions that our models will predict.

II. DESCRIPTION OF BASINS

Beneath the sea surface off Southern California there lie a series of mountain ranges and valleys (Figure 1). Mountain peaks break the ocean surface to form the offshore islands; valleys, some deeper than 2000 m, form isolated marine basins. High valley walls limit exchange of basin waters with the ocean ocean (Figure 2). Water that does enter from the open ocean at depths of 500 m or greater enters with low oxygen concentration. Oxidation of organic matter decreases the oxygen to a level where the inshore basins of Santa Barbara, San Pedro and Santa Monica have virtually no animal life in their depths (Figure 3).

The inshore basins are the most accessible for sludge disposal, the best studied and have in their depths the most depauperate fauna. The traditional definition of a marine basin is a bathymetric depression which is totally cut off from horizontal water exchange (e.g. Emery 1960) by mountain ridges or sills. Above the classical basin are additional volumes of water partially isolated from the open sea by ridges around part of the periphery; for our analysis, it is important to consider those as part of the basins also. The totally isolated part of a basin will be called the lower basin, the overlying water which is in a dead-end canyon will be known as the upper basin. Above this is water which flows easily over (or around) the physical obstructions, this will be called upper shelf water or flow through zone (e.g. see Figure 3). (See Appendix 2 for more discussion of this.)

The three basins most thoroughly discussed here are the Santa Barbara, Santa Monica and the San Pedro Basins. The Santa Barbara Basin has been the most extensively studied and has provided information on the basin mixing processes. Santa Monica and San Pedro Basins are closest

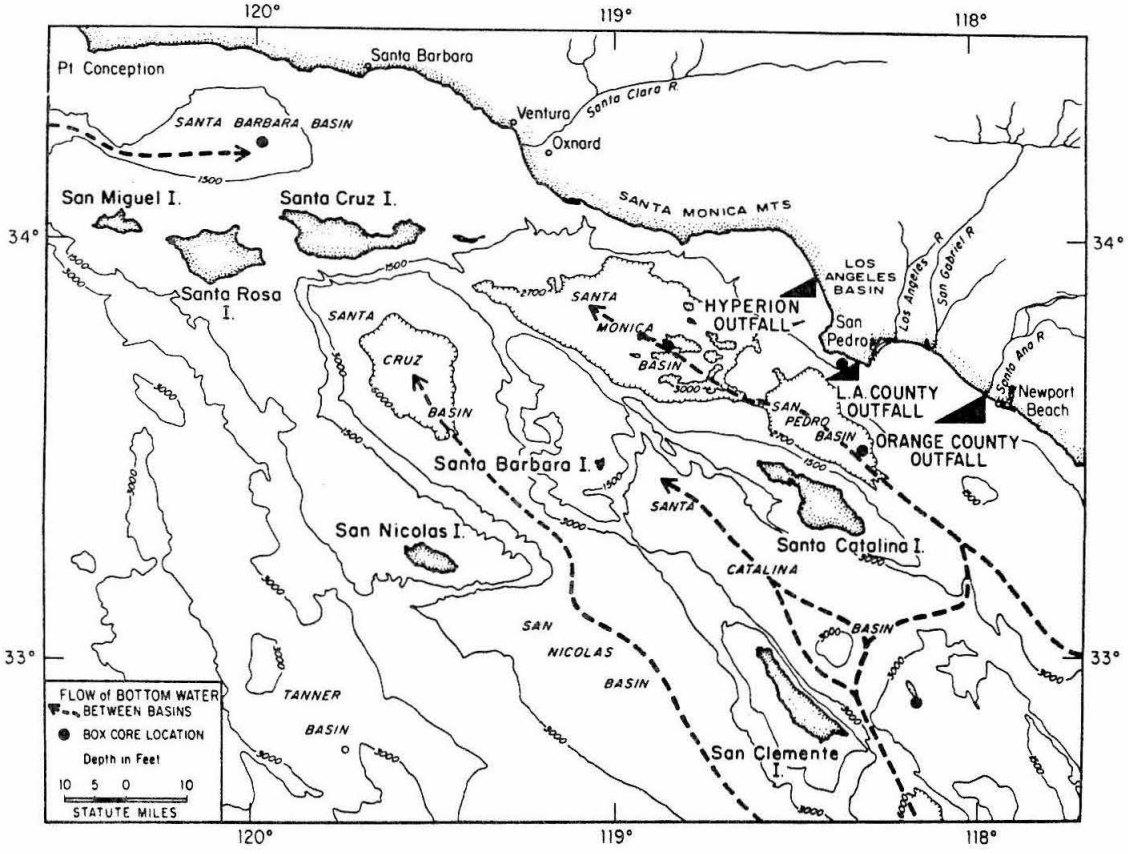

FIGURE 1

The Marine Basins of Southern California
(from Bertine and Goldberg, 1977)

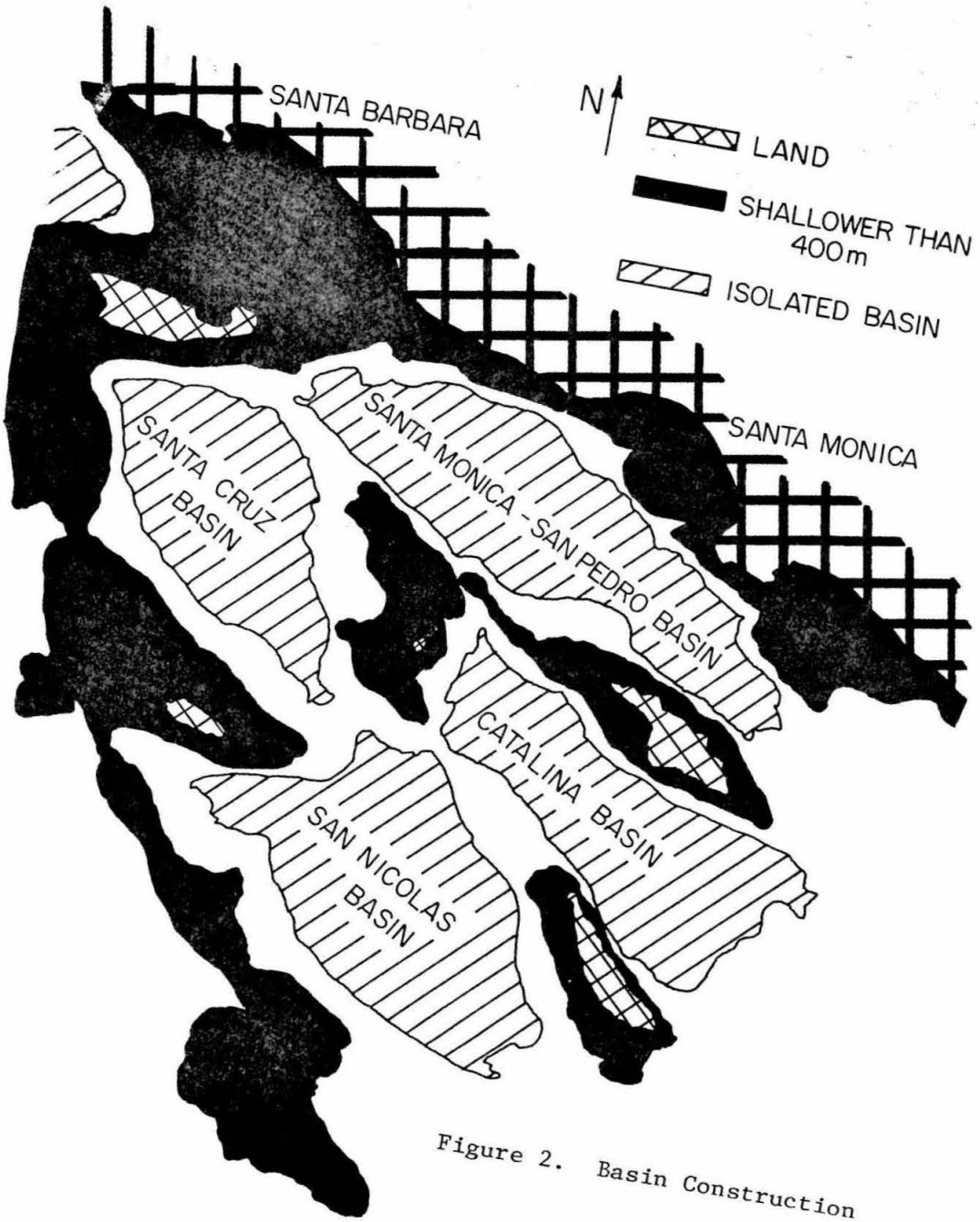

Figure 2. Basin Construction

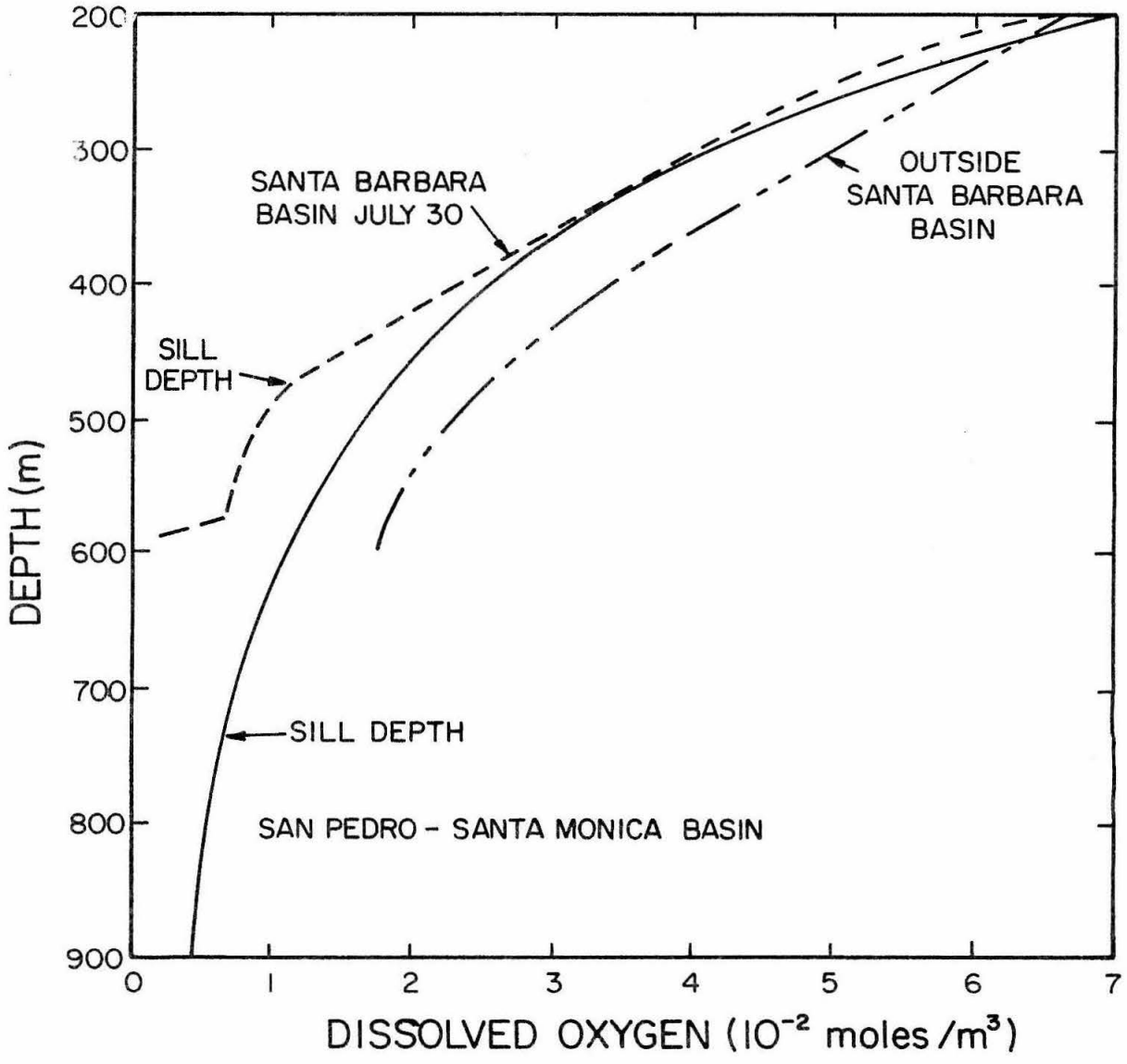

Figure 3. Oxygen Profiles Off Southern California

to the Los Angeles metropolitan area and are therefore the primary sites for basin disposal of sludge. Because the exchanges in the lower parts of these two basins are controlled by the same sill at the south end of San Pedro Basin and because vertical profiles of chemically-important quantitites suggest that the two basins are horizontally well mixed, we have considered them to be one basin (Figure 4, Table 1).

Basin sediments consist of interbedded layers of green claylike silts and coarser sands (Gorsline and Emery 1959, Hulsemann and Emery 1961). The clay and silt settles fairly uniformly throughout the basins; sand and coarse silt flow down from the coast through underwater canyons or are sloughed from shelf edges, settling out in the landward sides of the basins (Figure 5, curves 1,2,3 compared to 4 through 7). Sedimentation rates in the inshore basins range between 0.08 and 0.9 cm yr^{-1}. These are high compared to those in the outer basins of San Clemente and Santa Catalina, where 5 cm of sediment accumulate every 1000 years (Bruland et al. 1974, Bertine and Goldberg 1977).

Interstitial water deeper than a couple of centimeters is devoid of oxygen, high in sulfides and inhospitable for animals. Their absence keeps the top 10 cm layer from being stirred. As a result the sediments provide a record of the level of animal activity through time. Varves (sediment microlayers) and radioactive profiles indicate that the Santa Barbara and San Pedro-Santa Monica Basins are at present relatively devoid of animal life (Hulsemann and Emery 1961, Bertine and Goldberg 1977). Varving patterns in the Santa Barbara Basin indicate that periods of high and low sediment mixing alternate. Organism remains deposited in the two different phases also differ (Hulsemann and Emery 1961).

VERTICAL MODEL OF SANTA MONICA - SAN PEDRO BASIN

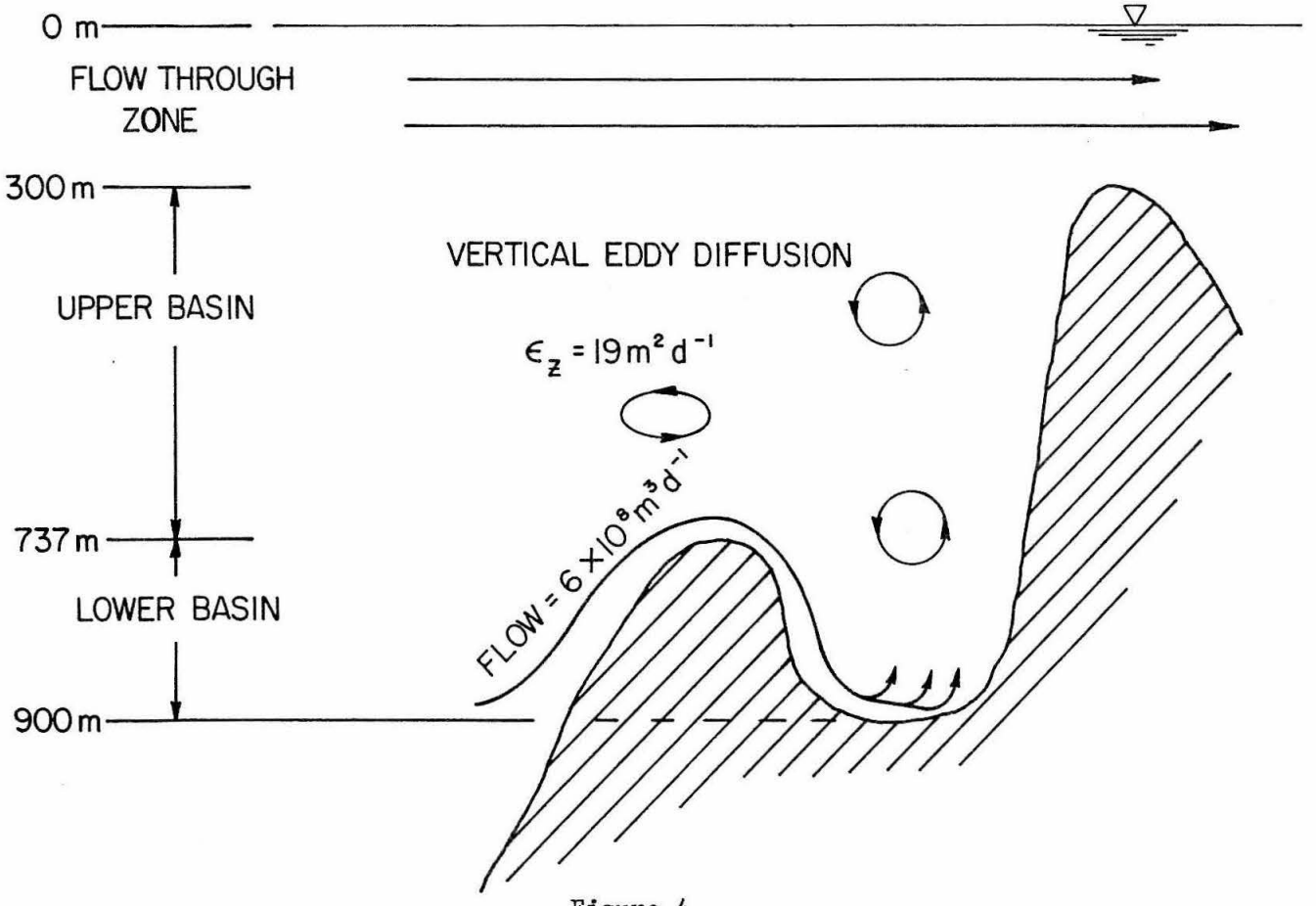

Figure 4

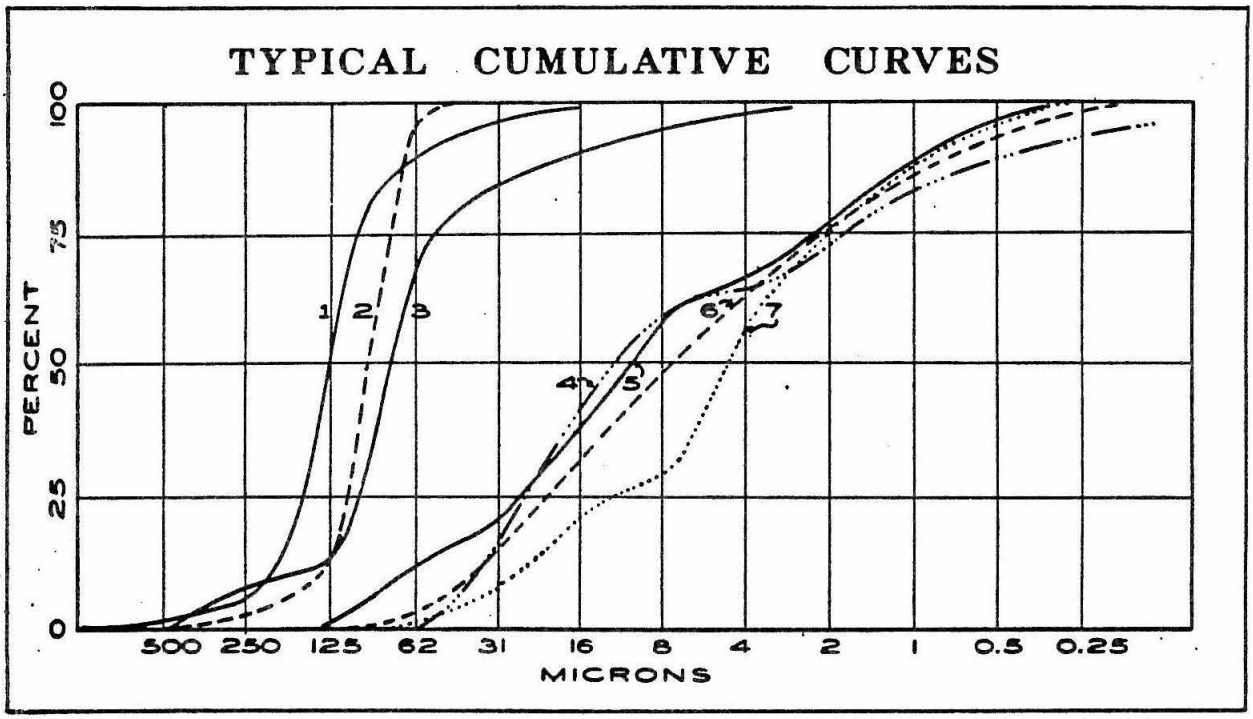

Figure 5. Typical size distribution curves for various samples from the San Pedro-Santa Monica Basin System.

(From Gorsline and Emery 1959)

TABLE 1

Nearshore Basins

	Santa Barbara	San Pedro-Santa Monica
Lower Basin		
Sill depth (m)	475.	737.
Maximum depth (m)	114.	165.
Average depth (m)	65.	118.
Area at sill (m^2)	6.6×10^8	$25. \times 10^8$
Volume (m^3)	4.3×10^{10}	$29. \times 10^{10}$
Upper Basin		
Depth at top (m)	250.	300.
Depth at bottom (m)	475.	737.
Area at top (m^2)	19×10^8	39×10^8
Volume (m^3)	31×10^{10}	149×10^{10}

The implication is that oxygen concentrations were periodically higher, permitting the sustenance of burrowing animals. Similar studies have reported historic evidence for animals reworking the San Pedro-Santa Monica Basin sediments but have not pursued the matter (Gorsline, 1958). Further study of basin histories could show what the mechanism for changes in basin circulation are, whether these are the same for the different basins, and how sensitive basins are to changes in organic inputs.

III. WATER EXCHANGE AND MIXING IN BASINS

The dominant basin water exchange mechanism is the fairly regular (but slow) influx of relatively dense water over basin sills. This high oxygen water flows down to the basin bottom, gradually displacing water upward and thereby causing new upward advection (see Appendix 2). Also important is the flux supplied by vertical mixing. These processes maintain the movement of water and its various associated substances to the lower basins. Oxygen concentration is determined by the balance of physical processes that supply oxygen and the chemical and biological processes that deplete it.

Upper basin circulation not only involves these vertical processes but also involves horizontal mixing processes. The rate of exchange horizontally depends on the size of the opening to an adjacent basin and on the horizontal eddy diffusion coefficient. Both factors can be expected to increase at shallower depths, but the size of the horizontal eddy diffusion coefficients is not known. Crude calculations suggest that, for modelling purposes, a one-dimensional model including vertical exchange, but assuming uniform properties in the horizontal, is adequate. Differences between open ocean and Santa Barbara Basin oxygen

concentrations at intermediate depths, however, support the idea that vertical processes are limiting (Figure 3).

A more dramatic type of basin circulation is the occasional overturn induced by sudden changes in density stratification. This was observed in Santa Barbara Basin by Sholkovitz and Gieskes (1971). Massive upwelling of open ocean water brings water denser than that in the lower basin over the sill and suddenly replaces much of the water in the lower basin. Oxygen concentrations near the basin bottom increased by a factor of four to levels sufficient to sustain more benthic animals. However, oxidation processes reduced these concentrations by half within a month.

Sholkovitz and Gieskes found evidence of previous overturns in Santa Barbara, although these occurred on an irregular basis. They found no evidence of their occurring in Santa Monica-San Pedro Basin. This overturn, dramatic though it was, does not seem to be the major factor in Santa Barbara Basin circulation.

IV. NATURAL FLUXES

Rates for various processes are shown in Tables 2 and 3. Note that almost all processes occur faster in Santa Barbara Basin than in San Pedro-Santa Monica when rates are normalized with respect to area. These include total sedimentation, water velocity, oxygen consumption and trace metal sedimentation rates.

Also note that heavy metal sedimentation rates have increased greatly as a result of anthropogenic processes. Bruland et al. (1974) suggest that the likeliest source for much of this is waste water discharge. Bertine and Goldberg (1977) examined sedimentation in marine

TABLE 2

Lower Basin Process Rates

	Santa Barbara	San Pedro-Santa Monica
Advective Flux		
Flow ($m^3\ d^{-1}$)	2.5×10^8	6×10^8
Vertical velocity at elevation of the sill ($m\ d^{-1}$)	0.38	0.2
Oxygen Consumption		
(moles d^{-1})	4.6×10^6	8×10^6
(moles $m^{-2}\ yr^{-1}$)	2.5	1.2
Silicate Regeneration		
(moles d^{-1})	6.5×10^6	-

TABLE 3

Sedimentary Inputs to Lower Basins
Values from Bruland, et al. (1974) and Hulsemann and Emery (1961)

	Santa Barbara			San Pedro-Santa Monica		
	Rates or Fluxes		TOTAL	Rates or Fluxes		TOTAL
	Natural	Anthropogenic	tons/year	Natural	Anthropogenic	tons/year
Sedimentation Rate						
mm yr^{-1}	4.			0.8	-	
gm-solids $m^{-2}yr^{-1}$	900.		600,000	260.	-	640,000
Fluxes						
organic carbon gm $m^{-2}yr^{-1}$	45.		30,000	13.		31,000
organic nitrogen gm $m^{-2}yr^{-1}$	3.		2,000	0.4		1,000
heavy metals mg $m^{-2}yr^{-1}$						
Pb	10.	21.	20	2.5	12	36
Cr	107.	29.	90	25.	28	130
Zn	97.	22.	80	30.0	20	123
Cu	26.	14.	26	11.	12	56
Ag	1.1	1.0	1.4	0.4	0.9	3.2
V	135.	78.	141	35.	20	135
Cd	1.4	0.7	1.4			
Mo			-	0.8	8	22
Ni	41.		27	15.		37
Co	10.		6.6	3.0		7
Mn	100.		66	240.		590
Fe	12,000.		7,900	30,000.		74,000
Al	17,000.		11,000	50,000.		120,000

basins more distant from the coast and decided that the considerably lower values found there were more suggestive of atmospheric fallout than of sewage discharge. Their conclusion did not explain the extremely high concentrations of some heavy metals found in Santa Monica-San Pedro Basin. It is still possible that the high anthropogenic fluxes there are the result of waste discharge.

V. SLUDGE INPUTS

Trace metals are predominantly in particulates in treated sewage effluents (both primary and secondary) discharged to the ocean (Chen et al. 1974; Morel, et al. 1974), and in digested sludge (Faisst, 1976). Theoretical calculations show that under reducing conditions of sewage, most trace metals can form sulfide or oxide precipitates (see Table 4).

Studies on the dissolution of sewage particulates are not consistent. Rohatgi and Chen (1975) found that more than half of the cadmium, zinc, and nickel had been released from sludge particulates five weeks after sludge had been mixed with seawater (Table 5). However, when Faisst (1976) performed similar experiments, he found that nickel was the only metal to solubilize to any measurable extent over a period of four weeks. Both sets of experiments did show that the majority of copper, chromium, lead, iron and manganese remained in particulate forms.

The fate of metals discharged into the ocean is linked with their particulate and dissolved distributions. For a strategy of containment, in which the goal of ocean discharge is to have the trace metals collect and stay in limited areas of the basin bottoms, it would be desirable for metals to settle quickly to the bottom, or be discharged as a denser-than-seawater mass on the bottom, with little release to the water column.

TABLE 4

Equilibrium Speciation in a Sludge Digester Organic Model[1]
pε = -4.40, pH = 7.9
(from Faisst, 1976)

			COMPLEXES[2]									SOLIDS	
	ligands →		CO_3	SO_4	Cl	NH_3	S	PO_4	SiO_3	CN	AC	OH		
	total conc →		1.60	---	2.38	1.63	2.03	2.42	3.78	3.81	1.78	---		
metals ↓		free conc →	3.48	2.93	2.38	2.82	11.4	8.40	10.0	6.23	1.78	5.91		
Ca	2.60	4.38	5.04	6.04	---	7.30	---	7.80	---	---	5.67	8.99	$Ca_3(PO_4)_2$	3.31
Mg	2.21	2.59	3.22	4.15	---	5.31	---	5.52	---	---	3.79	6.20	$Mg_2(PO_4)_2$	3.03
K	2.60	2.60	---	4.95	---	---	---	---	---	---	---	---		
Na	2.11	2.11	4.90	4.86	---	---	---	---	---	---	---	---		
Fe^{3+}	1.90	23.7	---	24.1	25.4	---	---	21.5	19.4	18.8	20.1	15.0	Fe_3O_4	2.63
Fe^{2+}	---	6.93	---	8.59	8.92	8.45	---	3.36	---	8.71	5.52	7.94	FeS	2.28
Mn	3.93	5.90	6.14	7.56	7.69	8.02	---	8.33	---	---	7.05	8.41	$MnCO_3$	3.94
Cu^{2+}	3.30	25.8	23.4	27.5	25.8	23.5	---	27.9	---	---	25.8	26.1	CuS	3.30
Cu^{1+}	---	19.2	---	---	18.7	14.0	---	---	---	8.13	---	---		
Cd	4.72	16.3	15.4	18.0	17.0	16.6	12.9	22.4	---	17.1	16.0	18.7	CdS	4.72
Zn	2.70	10.1	9.33	11.8	11.2	10.6	---	13.0	---	18.7	10.6	11.5	Zn	2.70
Ni	3.36	10.4	9.40	12.1	12.8	10.5	---	13.6	---	4.44	11.5	11.5	NiS	3.70
Pb	3.82	16.4	13.3	17.7	17.6	---	---	---	---	31.6	16.2	16.5	PbS	3.82
Ag	5.11	19.6	---	21.9	19.0	---	14.2	---	---	11.2	21.0	23.8	Ag_2S	5.41
Cr	2.86	10.8	---	12.5	13.1	---	---	7.78	---	---	---	3.66	$Cr(OH)_3$	2.94
H^+	---	7.9	1.63	9.09	---	1.66	5.75	4.46	3.79	5.12	4.88	---		

(1) All values as p[X] = -log (molar concentration of X).

(2) Concentrations of complexes are sums of all complexes of a given Metal Me, with a given ligand L. $\Sigma_{k,j} [Me_k L_j]$ where k,j are the stoichiometric coefficients.

TABLE 5

Percentage of Trace Metals Released After Five Weeks
From the Particles in Digested Hyperion Sludge
(from Faisst, 1976)

Metal	50:1 Dilution (1)	100:1 Dilution (1)	200:1 Dilution (1)
Cd	93.0	95.0	96.0
Cu	5.0	5.6	9.0
Cr	2.0	2.0	3.8
Fe	0	0	0
Mn	31.8	34.7	35.7
Ni	49.0	58.0	64.0
Pb	37.8	35.4	35.4
Zn	18.0	24.4	58.7

(1) Sludge was diluted with filtered natural seawater.

Source: Rohatgi and Chen, 1975.

For a strategy of dilution, trace metals should be widely enough dispersed so that: (a) the impact on the water column is minimal (i.e. by dissolution of metals during sludge particle sedimentation); and (b) the loading in natural sediments is light over a large area. Particle settling rates are an important factor in this. Faisst (1976) has measured sludge particle settling rates and found that the particles exhibit a broad distribution of settling velocities (Figure 6).

This range of sedimentation rates might represent the worst situation with regard to disposal in the marine basins because neither containment nor dilution works completely. A vertical flow of water will keep suspended those particulates with settling velocities less than the upward water flow velocity. At a vertical water velocity of 0.2 m d^{-1} calculated in the Santa Monica-San Pedro Basin at the level of the sill, approximately 30-40 percent of the sludge might stay suspended with the rest settling out (Figure 6).* If these are the fall velocities, then the strategy of containment in the lower basin might not work. However, if the sludge coagulates upon discharge, the settling rates would increase and the sludge would be taken to the bottom much more efficiently.

An alternative strategy for disposal in the marine basins would involve discharge in the upper basin or upper shelf waters. We are presently working on the development of a model to describe these processes.

The amounts of trace metals and oxygen consuming organics that can be expected if sludge were to be discharged into the basin are shown in Table 6. These numbers are the estimates of suspended solids to be

*A quartz particle of about 2μ sedimentation diameter would also settle at about 0.2 m d^{-1}.

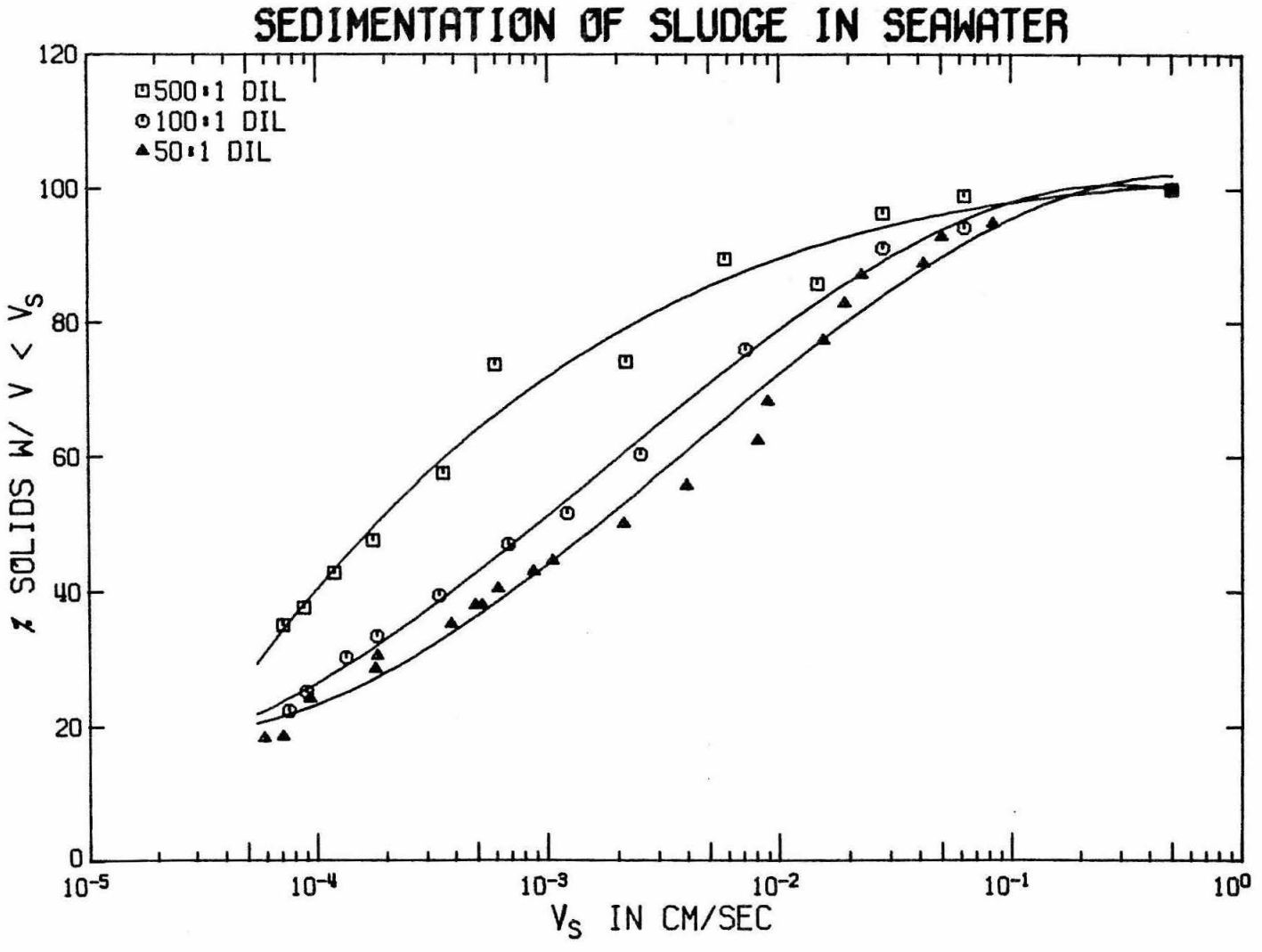

Figure 6. Sludge Particle Sedimentation Rates (from Faisst, 1976)

TABLE 6

Projected Discharges, 1985

	Los Angeles City	Sanitation Districts		Total
		Los Angeles County	Orange County	
Flow				
MGD[a]	330	400	225	955
$10^6 m^3 d^{-1}$	1.2	1.5	0.9	3.6
Suspended solids[a]				
Influent, tons d^{-1}	530	800	330	1660
Sludge, tons d^{-1}	270	530	160	960
BØD of sludge,[b] 10^6 moles $O_2 d^{-1}$	5.9	11.7	3.5	21
Heavy metals in sludge,[c] kg d^{-1}				
Cd	6	21	21	48
Cr (total)	560	1,236	263	2,060
Cu	400	776	402	1,590
Pb	27	326	120	470
Hg	3.0	1.4	0.4	4.8
Ni	162	210	81	453
Ag	23	15	14	52
Zn	594	2,592	372	3,600

a. Values taken from LA/OMA 1976.

b. BØD of sludge assumed to be sludge fraction of suspended solids x incoming BOD of 376 mg/1. 100 tons suspended solids = 2.2 x 10^6 moles O_2.

c. All metals removed in processing assumed to go to sludge. Influent concentrations and the removal efficiencies in SDLAC (1973) used to calculate L.A. County contribution, in DPWCLA (1973) used to calculate L.A. City contributions, and influent concentrations in CSCOC (1973) and DPWCLA (1973) removal efficiencies used to calculate Orange County contributions.

TABLE 7

Comparison of Lower Santa Monica-San Pedro
Basin Sedimentation with Projected Sludge Discharge

Substance	(A) Lower SM-SP Basin Flux(1)	(B) Projected Sludge Discharge	B/A
Organic C (BOD moles - O_2)	2.6×10^9 (2)	7.7×10^9	3
Heavy Metals (tons/yr)			
Cd	(1.4)	18	13
Cr	130	750	6
Cu	56	580	10
Pb	36	170	5
Hg	-	1.8	-
Ni	37	165	4
Ag	3	19	6
Zn	123	1,300	11

(1) From Table 3, total present fluxes including anthropogenic.

(2) Assuming complete oxidation of all C.

discharged in 1985. Table 7 gives a comparison of projected sludge outputs of metals to the present estimates of trace metal accumulation rates in the sediments of the lower Santa Monica-San Pedro Basin; the ratios range from 3 to 13 times as great.

VI. A SIMPLE MODEL FOR THE EFFECT OF SLUDGE DISPOSAL

The potential impact on sludge disposal in the lower basin can be estimated by using simple box models of the lower Santa Barbara - Santa Monica Basin. Such a model was used to determine the present rate of oxygen utilization in the lower basins and can be used to estimate the impact of suspended sludge on oxygen and trace metal concentrations.

Input to this model basin is through water flowing in over the sill, by eddy diffusion at the sill, and by sludge discharge; outflow is by water advection upward at the sill, by chemical reaction, or possibly by eddy diffusion. Fates of oxygen and organic carbon are intertwined by their mutual consumption in oxidation of organics.

The equations used to describe this model are shown in Table 8. They were solved for steady state conditions for the sludge inputs shown in Table 7. Neither sedimentation nor solubilization characteristics were considered; rather all material inputs are considered distributed over the water column with no sedimentation. The resulting concentrations are then upper limits as some sludge inputs will undoubtedly become part of the bottom sediments.

Actual concentration changes that would occur with sludge discharge can be expected to be greater near the discharge than those calculated

TABLE 8

Box Model for Oxygen, Organic Matter, and Trace Metal Concentrations in Lower Santa Monica-San Pedro Basin.

Equations (a) and (b) describe concentrations of oxygen and organic carbon. Equations for trace metal concentrations are analogous to equation (b) without the chemical reaction term, with concentration in incoming water the same as that of water above the sill, and with sludge input of metals in place of $B\emptyset D_{in}$.

The concentration gradient is approximated as the difference between concentration inside and above the lower basin divided by a mixing distance. The steady state solutions (Table 9) correspond to $\partial O_i/\partial t = \partial C_i/\partial t = 0$.

For oxygen

$$V \cdot \frac{\partial O_i}{\partial t} = \text{bottom advection} + \text{diffusion flux} - \text{top advection} - \text{chemical reaction}$$

$$= Q\,O_B + \varepsilon_z\,A\,\frac{(O_T - O_i)}{\Delta z} - QO_i - rVC_iO_i \qquad \text{(a)}$$

Likewise, for organic carbon,

$$V\,\frac{\partial C_i}{\partial t} = QC_B + \varepsilon_z\,A\,\frac{(C_T - C_i)}{\Delta z} - QC_i - rVC_iO_i + B\emptyset D_{in} \qquad \text{(b)}$$

where

V = volume of basin = 2×10^{11} m^3

A = area at sill depth = 2×10^{9} m^2

Q = advective flow = 5×10^{8} $m^3\ d^{-1}$

ε_z = vertical eddy diffusivity = 19 $m^2\ d^{-1}$

r = reaction rate constant = 1.4 $m^3\ d^{-1}\ mole^{-1}$

O_T = oxygen concentration above the sill = 7.2×10^{-3} moles m^{-3}

O_B = oxygen concentration in incoming water = 1.5×10^{-2} moles m^{-3} $\simeq$ 0.3 ml l^{-1}

O_i = oxygen concentration in lower basin

C_T = organic carbon concentration above the sill (in oxygen equivalents) = 1.3×10^{-2} moles m^{-3}

C_B = organic carbon concentration in incoming water = 0 mole m^{-3}

C_i = organic carbon concentration in lower basin

$B\emptyset D_{in}$ = sludge input of organic carbon = 2×10^{7} moles d^{-1}

Δz = mixing distance at sill = 15 m.

TABLE 9

Effect of sludge disposal on concentrations in water in lower San Pedro-Santa Monica Basin. C_o is concentration with no sludge discharge, numbers from Morgan and Sibley (1975). C_s is concentration predicted by box model described in Table 8.

Element	pC_o - log conc (moles m^{-3})	Loading tons/year	pC_s - log conc (moles m^{-3})	$\frac{C_s}{C_o}$
Oxygen	2.30	-	2.42	0.76
Organic carbon	2.14	7700*	1.89	1.75
Cd	6.35	18	6.22	1.3
Cr (total)	6.02	750	5.0	15
Cu	4.33	580	4.22	1.2
Pb	6.89	170	6.05	7.2
Hg	6.60	1.8	6.52	1.03
Ni	4.47	165	4.40	1.08
Ag	6.43	19	6.30	1.4
Zn	4.12	1300	4.00	1.25

*Organic carbon loading given as 10^6 moles of oxygen equivalent per year.

with this model and to be less near the sill boundary. Concentrations in the upper basin cannot be expected to maintain the constant values at the sill that are assumed in this model.

Model results do show the magnitude of expected changes in concentrations in the water in the lower basin (Table 9). Concentrations of lead, chromium and organic carbon can be expected to increase significantly, concentration of oxygen to decrease. More detailed results will be presented from the one-dimensional model in a later report.

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APPENDIX 1
CHEMICAL REACTION RATES

I. INTRODUCTION

Introduction of sludge into seawater initiates a series of biologically-mediated reactions as the various oxidants in seawater are reduced by the sludge and subsequently re-oxidized in the water around them. Thermodynamic considerations predict the energetics of the various electron transfer reactions but kinetic and stoichiometric considerations determine their relative importance. Thus, in a closed aqueous system containing organic matter, its oxidation proceeds with reduction of O_2, then of NO_3^-, followed by that of NO_2^-. These will be followed by the reduction of MnO_2, FeOOH and eventually of SO_4^{2-} (Stumm and Morgan 1970). Concentrations of manganese and iron in oceanic waters are approximately 4×10^{-8} M and 2×10^{-7} M, respectively, small compared to oxygen (5 - 30 μM in the basins), nitrate (30 μM), and sulfate (0.028 M). For this reason, metal reduction reactions have been neglected in this study.

Thermodynamically most favored reactions are not always the important ones. Nitrate reduction is energetically less favorable than oxygen reduction until oxygen concentration reaches 10^{-12} M, but nitrate reduction has been reported when oxygen concentrations reach 5×10^{-6} M. An obvious interpretation is that the supply rate to an organism becomes more important than the absolute concentration of an oxidant. Thermodynamic information, then,will be used to determine the

ordering of different reduction reactions but must be used in conjunction with rate data to predict the effect of sludge disposal in oceanic basins. This appendix surveys the available relevant data.

One environmentally important property of sludge is its reduced nature and the accompanying high oxygen demand. Muellenhof (1977) reports that the five-day BOD of anaerobically digested sludge is usually between 2000 and 3000 mg/1. The BOD of the effluent-sludge mixture discharged by the Los Angeles City Sanitation District sewage treatment plant at Hyperion through the 7-mile outfall is 1900 mg/1 and the chemical oxygen demand (COD) is 7700 mg/1 (SCCWRP 1975). Such oxygen demands are high compared to seawater oxygen concentrations, which are as low as 0.14 mg/1 (4.5 μM) in the San Pedro Basin. Depletion of oxygen in seawater results in nitrate reduction and, eventually, sulfate reduction. Rates of these processes are the subject of the following sections.

II. REDUCTION REACTIONS

II-A. AEROBIC SLUDGE STABILIZATION

Myers (1974) established upper and lower limits for the decomposition rate of particles in mixed primary and secondary effluent from the Hyperion treatment plant. The ratio of particulate organic carbon concentration at a given time (t), to the initial concentration is given by f(t). Values of f(t) were fit to the equation:

$$f(t) = f_R + (1-f_R)\, e^{-kt} \qquad (1)$$

where f_R is the fraction of refractory organic carbon and k is a first order rate constant. The parameters in Table 10 provide upper and lower limits for the first order rate constant and the fraction of organic carbon refractory under aerobic conditions at 17°C. Values of k range from 0.05 to 0.22 day^{-1}.

TABLE 10

Upper and Lower Limits for Parameters of Equation (1) at 17°C

Decay Limit	Approximate F* Initial Rate	Approximate f_R	Estimated k
upper	0.088 day^{-1}	0.60	0.22 day^{-1}
lower	0.013 day^{-1}	0.75	0.05 day^{-1}

Muellenhof (1977) observed stabilization rates of anaerobically digested sludge under both aerobic and anaerobic processes in seawater at different hydrostatic pressures. The parameters f_R and k, derived from fitting the data to eqn. 1, are shown in Table 11. Statistical analysis of values for f_R and k shows that there is a significant difference between their values under aerobic and anaerobic conditions but there is no significant difference between their values at one and at 34 atmospheres.

*From Myers (1974)

$$F = \text{Initial rate } \left.\frac{d[f(t)]}{dt}\right|_{t=0} = -k(1-f_R)$$

TABLE 11

Rate Constants and Fraction of Non-biodegradable Organic Carbon for Muellenhof's Decomposition Experiments

Experimental* Conditions	k ($days^{-1}$)	f_R	Duration of Experiment (days)
Aerobic			
1 atmosphere	0.042	0.689	20
34 atmosphere	0.042	0.699	20
34 atmosphere	0.036	0.692	170
Anaerobic			
1 atmosphere	0.020	0.899	20
34 atmosphere	0.022	0.907	20
34 atmosphere	0.015	0.917	130

*All experiments were run at a temperature of 23°C. From Muellenhof (1977).

Muellenhof's (1977) value for the fraction of organic carbon that is not biodegradable, (∿70%), falls within the range established by Myers (1974) for effluent particulates, and his value for the rate constant is slightly below Myers' lower limit of .05 per day. Thus, the results of these two authors show satisfactory agreement considering the difference in their experimental conditions and material (effluent particles versus anaerobically digested sludge).

These carbon consumption rates can be compared with oxygen consumption of digested sludge measured by Muellenhof (1974). The laboratory measurements were made on a 2 centimeter thick sludge bed in a tank in which sea water was circulated and in which a dissolved oxygen sensor continuously monitored oxygen concentration. The in situ measurements were made on a twelve meter by sixty meter sludge bed,

which ranged from 0 to 1 centimeters thick, and was found at a depth of 15 meters. The ambient temperature of the sea water was 23°C over the several day duration of the measurements. The oxygen uptake measurements were made using two acrylic hemispherical domes, each equipped with a dissolved oxygen sensor and a stirrer. The results of these measurements are reported in Table 12, and they are compared with sludge stabilization rates using the expression of Muellenhof (1977) in Table 13. Lack of information on system geometry precluded calculations of initial oxygen uptake rates for laboratory experiments.

TABLE 12

Oxygen Uptake Rates for Digested Sludge
(from Muellenhof 1974)

	Sludge Description	Initial Rate ($g-O_2/m^2/day$)	Rate at a Later Time ($g-O_2/m^2/day$)
Laboratory Measurement	Corvallis Wastewater Treatment Plant (Oxygen)	2.72	0.98 at t = 53 days
Laboratory Measurement	Nassau County Sewage Treatment Plant Fast Rackway, N.Y.	0.72	0.55 at t = 20 days
In Situ Measurements	Anaerobically digested sludge	2.51	1.68 at t = 2.9 days (70 hrs)
In Situ Measurements	Aerobically digested sludge	3.74	2.0 at t - 2.7 days (65 hrs)

The agreement between measured and calculated oxygen utilization rates indicates that Muellenhof's (1977) rate constant can be used to obtain an estimate of the rate of oxygen uptake by digested sludge.

TABLE 13

Comparison of oxygen utilization rates as measured by Muellenhof (1976) with sludge stabilization rates calculated from the expression of organic matter concentration versus time reported in Muellenhof (1977).

Source of Sludge	Initial Oxygen(1) Utilization Rate	Initial Sludge(2) Stabilization Rate	$\frac{\text{Rate at time = t}}{\text{Rate at time = 0}}$ (3) Measured	Calculated
Anaerobically digested sludge: In situ Measurement	0.025 mole-O_2/day	0.03 mole-C/day	Ratio = 0.67 (at t = 3 days)	Ratio = 0.89
Corvallis Treatment Plant Oregon	-	-	Ratio = 0.36 (at t = 53 days)	Ratio = 0.12
Nassau Co. Treatment Plant	-	-	Ratio = 0.76 (at t = 20 days)	Ratio = 0.45

(1) The measured initial oxygen utilization rate = 2.5 g-O_2/m^3/day. One hemisphere was 76 cm in diameter and the other was 50 cm in diameter. Area covered by 76 cm diameter hemisphere = 0.45 m^2; Area covered by 50 cm diameter hemisphere = 0.20 m^2. Taking 0.3 m^2 as an intermediate value, O_2 utilization rate/hemisphere = $(2.5\text{g-}O_2/m^2/\text{day})(0.3m^2)(\frac{1\text{mole}O_2}{32\ \text{g-}O_2})$.

(2) The calculated initial sludge stabilization rate [denoted R(t=0)]: $R(t=0)=KC_0=(0.04\text{day}^{-1})(0.3)(10\ \frac{\text{g-C}}{\ell})=0.2\text{g-C}/\ell/\text{day}$; where $10\frac{\text{g-C}}{\ell}$ is the initial concentration of organic carbon, 0.3 of which is biodegradable. Assuming a 1 cm thick sludge bed, the volume of sludge per hemisphere is about $(1\text{ cm})(.3m^2)(10^4\ \frac{cm^3}{m^2})(10^{-3}\ \frac{\ell}{cm^3}) \simeq 3\ell$. Thus the R(t=0) = $(0.12\text{g-C}/\ell\ \text{day})(3\ell)=0.36\text{g-C/day}$ or 0.03 moleC/day.

(3) $R(t=0) = -KC_0$, and the rate at a time, t, denoted R(t) is: $R(t) = KC_0\ e^{-Kt}$. Thus $\frac{R(t)}{R(t=0)} = \frac{KC_o\ e^{-Kt}}{KC_0} = e^{-Kt}$.

II-B. ANAEROBIC SLUDGE STABILIZATION AND SULFATE REDUCTION

Muellenhof's (1977) experimental design for the measurement of the first order rate constant for the process of sludge stabilization and sulfide production under anaerobic conditions are described in Section II-A and his results are reported in Table 11. The values for the fraction of organic carbon that is not biodegradable are only approximate because of the relatively short 20 day reaction time; a 130 day experiment established that the fraction is probably close to 0.9. Maximum total dissolved sulfide concentration observed was 16 mM (Muellenhof 1977). The rate constant for anaerobic stabilization of digested sludge is about one-half of the aerobically-obtained rate constant at the same temperature (23°C). The sulfide production rate can be obtained by assuming a stoichiometry for the oxidation of sludge by dissolved sulfate which, as will be discussed below, is probably close to 2 moles of carbon consumed per mole of sulfide produced.

Berner (1974) has discussed the oxidation of organic matter with concomitant sulfide production in anoxic sediments. He modeled the depth distribution of dissolved sulfate using the processes of diffusion, advection and sulfate reduction. The rate of sulfate utilization was assumed proportional to the concentration of organic matter usable by sulfate reducing bacteria, (defined as G_s):

$$\frac{-d[SO_4^{=}]}{dt} = k_s G_s$$

where k_s is a rate constant (note that this expression is similar to those used by Myers, 1974, and Muellenhof, 1977). Values for k_s and

G_s estimated by Berner (1974) for three cores are presented in Table 14. Values for the rate constant are at least an order of magnitude lower than that measured by Muellenhof (1977). This could be due to, among other factors, differences in the nature of anaerobically digested sewage sludge and the organic matter deposited in sediments derived from natural marine sources, especially with respect to nutrient content. One might expect the higher nutrient content of digested sludge to support a larger population of bacteria than sedimented organic matter, which has undergone degradation in the water column.

II-C. THE EFFECT OF TEMPERATURE ON SLUDGE STABILIZATION RATES

Myers (1974) measured the rate of decomposition of effluent particles in sea water at three temperatures: 35°C, 17°C, and 2°C. The rate constant at 17°C was 0.12 per day, and at 2°C was 0.012 per day. Thus, based on one experimental run for each temperature, a drop in temperature of 15 degrees decreases the rate constant by an order of magnitude. This is a much larger temperature effect than one would expect from a typical biological Q_{10} value of 2, (Lehninger, 1970). For such a Q_{10} the rate should decrease by no more than a factor of three or four for the same drop in temperature. Clearly, Myers (1974) experiment was designed to obtain a semi-quantitative idea of the temperature effect. A more reasonable estimate would be that rates at 23°C are a factor of four or five times greater than the rates at 8°C.

TABLE 14

Values for the rate constant and biodegradable organic matter concentration applicable to sulfate reduction from three marine sediment cores (Berner 1974)

CORE LOCATION	k_s (day^{-1})	G_s
Santa Barbara Basin	6.5×10^{-6}	2.5×10^{-1} mole-C/ℓ
Somes Sound, Maine	4.8×10^{-4}	1.8×10^{-1} mole-C/ℓ (0.8% by weight)
Long Island Sound, Conn.	1.6×10^{-4}	1.3×10^{-1} mole-C/ℓ (.62% by weight)

II-D. REDUCTION OF NITRATE

With the depletion of oxygen, nitrate becomes the dominant oxidizing agent. There is extensive evidence for denitrification in low oxygen containing oceanic areas. Fiadeiro and Strickland (1968) suggested that denitrification becomes important when oxygen concentrations are lower than 0.2 ml/ℓ (9μM). Work by Goering and Cline (1970) suggests that the crucial value is closer to 0.1 ml/ℓ (4.5 μM). The oxygen concentration range of 0.1-0.2 ml/ℓ is also the range where midwater crustacean respiration rates start to show a dependence on oxygen concentration (Childress 1975).

We have assumed an oxidation rate of organic matter constant for oxygen concentrations greater than 5μM, and linearly related to oxygen plus nitrate concentrations when oxygen is less:

$$r = \text{rate of oxidation} = K, \text{ if } [O_2] \geq 5\mu M$$

$$= K \frac{[O_2] + [NO_3]}{A+B}, \text{ if } [O_2] \leq 5\mu M$$

where A = 5μM

B = 30μM, the background nitrate concentration in the basin.

If the nitrate is being reduced to N_2, each nitrate will accept 5 electrons. If $\underline{r}$ is given in terms of oxygen-equivalents, the rate of nitrate reduction will be $4/5\ r \frac{[NO_3]}{A+B}$. The rate of oxygen reduction then will be $r \frac{[O_2]}{A+B}$.

II-E. CONCLUSION

Oxidation rates of sludge organic matter will depend on concentrations of organic matter, oxygen, nitrate and sulfur. Our approach has been to assume different oxidation rates and reductants at various oxygen concentrations.

The basin oxidation expression is

$$\frac{dC}{dt} = -r[O_2]\ C$$

where

C = reactive organic carbon concentration, in oxygen equivalents

$[O_2]$ = oxygen concentration

$$r(O_2) = 0.01\ day^{-1} \text{ if } [O_2] \geq 5\mu M$$

$$= 0.01\ \frac{[O_2] + [NO_3]}{A+B} \text{ if } 5\mu M \geq [O_2] \geq 1\mu M$$

$$= 0.002\ day^{-1} \text{ if } [O_2] < 1\mu M$$

A = 5μM

B = 30μM

The oxidation rate for oxygen concentrations less than 1μM is the anaerobic rate of $0.005\,day^{-1}$ corrected for the fact that one third of the organic matter is degraded in sulfate reduction.

III. THE OXIDATION OF AQUEOUS AMMONIA*

Muellenhof (1977) reports that the range in the ammonia concentration for digested sludge from Bay Park Water Pollution control plant is from 550 to 850 milligrams per liter, and SCCWRP (1975) reports that, for the effluent-sludge mixture discharged from the seven mile pipe from LACSD, the aqueous ammonia concentration is about 300 milligrams per liter. This constitutes a chemical oxygen demand of 1400 milligrams per liter. Nitrifying bacteria, (chemoautotrophs), isolated from the marine environment have been shown to oxidize ammonia at very low concentrations of dissolved oxygen, (Gunderson, 1966).

Carlucci and Strickland (1968) studied the effect of temperature and substrate concentration on the growth constant of bacteria that they had collected from the North Pacific. None of the cultures isolated oxidized ammonia at 5°C over the three month duration of their experiments. On the other hand, they point out that some of the isolates had been collected from waters whose late summer temperature is as low as 9°C, and that a culture isolated from sub-artic waters oxidized ammonia "very readily" at 12°C after a fifty day lag period. Thus, while quantitative data is lacking on the rate of oxidation of aqueous ammonia at low temperatures and low oxygen concentrations, it is probably much slower than that of digested sludge so that the effect of ammonia oxidation on the oxygen concentration is probably small.

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*Aqueous ammonia as used here refers to ammonium ion as well as to dissolved ammonia.

IV. THE OXIDATION OF AQUEOUS SULFIDE BY DISSOLVED OXYGEN

Oxidation of aqueous sulfide by oxygen in sea water is a complex process with an as yet unknown mechanism. Chen and Morris (1972a, b) studied the effect of pH, initial sulfide concentration and initial oxygen concentration on the reaction rate at low ionic strength. Cline and Richards (1969) studied the reaction kinetics in sea water. In addition, workers at Woods Hole have investigated the effect of bacteria on the sulfur cycle in the ocean. The investigations of the kinetics of the reaction of aqueous sulfide with dissolved oxygen will be discussed in Section IV-A and biological aspects will be discussed in Section IV-B.

IV-A. THE KINETICS OF THE REACTION OF DISSOLVED OXYGEN WITH AQUEOUS SULFIDE

Chen and Morris (1972a) and Cline and Richards (1969) noted that sulfide oxidation kinetics are complex with an induction period of from .5 to 5 hours. Table 15 shows that there are several conceivable products of the reaction, ranging in oxidation state from zero, (elemental sulfur and polysulfides) to plus six (sulfate ion).

TABLE 15

Possible Pathways for the Reaction of Aqueous Sulfide and Dissolved Oxygen

aHS^-	+ b O_2	=	products	$Rc \equiv \frac{a}{2b}$
HS^-	+ $2O_2$	=	$SO_4^=$ + H^+	0.25
$2HS^-$	+ $3O_2$	=	$2SO_3^=$ + $2H^+$	0.33
$2HS^-$	+ $2O_2$	=	$S_2O_3^=$ + H_2O	0.5
$2HS^-$	+ O_2	=	S° + $2OH^-$	1.0

TABLE 15
(continued)

$S^\circ + SO_3^{2-} = S_2O_3^{=}$

$HS^- + SO_3^{=} + 1/2\ O_2 = S_2O_3^{=} + OH^-$

$H_2O + S_2O_3^{=} = SO_4^{=} + S^\circ + 2H^+$

$HS^- + S^\circ = S_2^{=} + H^+$

$S_2^{=} + S^\circ = S_3^{=}$ etc.

} Polysulfide formation

$nHS^- + \left(\frac{n+5}{2}\right)O_2 + (n-2)\ H^+ = S_nO_6^{2-} + (n-1)H_2O$ generalized reaction for polythionate formation.

In their kinetic studies of the reaction of 25°C, Chen and Morris (1972a) varied the initial sulfide concentration from 50 to 200 μM, the initial oxygen concentration from 160 to 800 μM, and the pH from 6 to 13. They followed the oxygen concentration, the sulfide concentration (both spectrophotometrically and colorimetrically), and occasionally determined elemental sulfur, thiosulfate, sulfite, polysulfides and polythionates in the reacted mixture. They expressed their results in terms of the following rate law:

$$-\frac{d[S_T^{2-}]}{dt} = k[S_T^{2-}]^{1.34}\ [O_2]^{0.56}$$

where k is a rate constant and has units of $M^{-0.9}$ $hour^{-1}$. This rate law describes the course of the reaction directly following the induction period. The rate constant is strongly dependent on pH and weakly dependent on the initial concentrations of dissolved oxygen and total sulfide.

The rate constant, k, has maxima at pH's of 8 ($k = 22\ M^{-0.9}\ hour^{-1}$) and 11, minima at pH's of 6 (k=0) and 9 ($k=6\ M^{-0.9}\ hour^{-1}$). At a pH of 7, k is about $5\ M^{-0.9}\ hour^{-1}$. Thus, changes in pH from 8 to either 7 or 9 decrease the rate by a factor of four to five (Chen and Morris, 1972a). pH affects

duration of the induction period and product distribution as well as the rate constant. The induction period is 0.5 hours at pH's of 8 and 11, 6 hours at a pH of 7, and 2 hours at a pH of 9. Thus, the lag time is smallest at the pH values where the rate constant is largest. Maximum amounts of polysulfides are formed at a pH of 8. At pH values above 8.5, thiosulfate is the major product. At neutral and acid pH's, the major product is polysulfide when oxygen is in excess, elemental sulfur when it is not (Chen and Morris, 1972a).

Cline and Richards (1969) expressed the results of their sea water experiments in terms of the rate law

$$- \frac{d[O_2]}{dt} = k'[O_2][S_T^{=}],$$

where k' is the apparent rate constant, 1.5×10^{-3} μM^{-1} $hour^{-1}$. The rate constant of Chen and Morris (1972a) for approximately the same conditions is about 20 $M^{-0.9}$ $hour^{-1}$ or 2.0×10^{-5} μM^{-1} $hour^{-1}$. This discrepency will be discussed in the last section. Cline and Richards also reported an induction period of about one hour.

The product distribution in the presence of an excess of dissolved oxygen indicated that thiosulfate was the major product under their conditions. They stated that a low concentrations of oxygen, (below 2 or 3 μM), the products tend toward lower oxidation states, but they could not detect elemental sulfur and did not analyze for polysulfides.

Cline and Richards (1969) calculated that the reaction rate should halve for a ten degree drop in temperature by using the Arrhenius

activation energy equation. They noted that this agreed with the data of Avarahami and Golding (1968), whose work was done under substantially different experimental conditions (i.e., pH's of 11 to 13, temperatures from 25 to 55°C, and total sulfide and dissolved oxygen concentrations of from 100 to 1000 μM as contrasted to pH's between 7.5 and 7.8, oxygen concentrations of 30-240 μM and a temperature of 10°C.

Divalent transition metal ions, (Mn(II), Co(II), Ni(II), Cu(II)) and the alkali earth metals (Ca(II) and Mg(II)) increased the rate of the reaction by as much as two orders of magnitude, depending on their concentration and the pH (Chen and Morris, 1972b). Cline and Richards (1969) found that the 5 μM Fe(II) increased the rate slightly under their experimental conditions, (which include an ionic strength of about 0.7). Chen and Morris (1972b) found that Ni(II) had the most pronounced effect, increasing the rate by a factor of ten at a concentration of 10 μM and a pH of 8.65. Mg and Ca at concentrations of 1 mM increased the reaction rate by a factor of five for a pH of 8.6. Both investigations found that the presence of certain organic compounds inhibited the reaction, but only rarely did the presence of an organic compound decrease the rate by more than a factor of two. The most pronounced inhibitory effect was observed with cyanide ion, which decreased the reaction rate by a factor of ten when present at concentrations above 20 mM. The results of these catalysts and inhibition studies indicate that, while metal ions can significantly increase the rate when present at low concentrations, nothing significantly decreases the rate unless present at relatively high concentrations.

IV-B. THE ROLE OF BACTERIA IN THE OXIDATION OF AQUEOUS SULFIDE

Bacteria capable of oxidizing aqueous sulfide, elemental sulfur and aqueous thiosulfate are present in the open ocean, in coastal waters, in the waters of anoxic basins, and in anoxic sediments, (Tuttle and Jannasch 1972, 1973, 1976).

Tuttle and Jannasch (1972) tested marine bacteria isolates for the ability to oxidize sulfide and thiosulfate. Most strains grew more efficiently on a sulfide substrate than a thiosulfate substrate (only 19% of the isolates oxidized more than 5% of the thiosulfate in the medium and only one strain was able to attack elemental sulfur). Half of the isolates were found to be similar to T. trautweinii, and the authors point out that the inclusion of this strain in the thiobacillus species has been "justifiably disputed." This facultative autotrophic species, along with certain other strictly heterotrophic bacteria oxidizes thiosulfate to polythionates. Whether this metabolic pathway can provide sufficient energy to support autotrophic growth is not certain. However, the authors point out that sufficient energy might be available if high concentrations of thiosulfate are present. The isolates similar to T. trautweinii were able to grown in an inorganic medium, which suggests that they are capable of chemotrophic growth.

None of the isolates found by Tuttle and Jannasch (1972) were obligative autotrophes. Several strains oxidized more thiosulfate in the presence of organic substrate than in its absence. The authors found acidophillic thiobacilli only in near shore environments. They concluded by saying that the fact that 30% of their strains grew on

sulfide indicates that participation in the process of oxidation of aqueous sulfide to sulfur by organisms could be significant in sulfide turnover in the marine environment. Whether bacterial oxidation of sulfide can compete with chemical oxidation under aerobic conditions is a key question.

Tuttle and Jannasch (1976) measured thiosulfate utilization rates of bacterial isolates under conditions of low temperature and both low and high pressure. They had one strain with an average rate of thiosulfate utilization at 2°C and 5300 meters depth of 1.3 $\mu M\ day^{-1}$. The thiosulfate utilization rate near the sea surface was 266 - 300 micromolar per day for 22 day experiments with sea water and sea water plus 10 mM potassium nitrate as media. Based on the known metabolic pathways of the axenic cultures used, the authors concluded that tetrathionate must have been the product of the oxidation of thiosulfate.

IV-C. DISCUSSION AND CONCLUSION

Rates of aqueous sulfide oxidation by dissolved oxygen as calculated from the expressions of Cline and Richards (1969) and Chen and Morris (1972a) are compared in Table 16 for various concentrations of dissolved oxygen and total sulfide. Also compared are the rates as calculated with the expression of Chen and Morris (1972a) and those calculated with the same rate constant but assuming that the reaction is first order with respect to the concentrations of the reactants (recall that Chen and Morris (1972a) found the reaction to be of an order 1.34 for total sulfide and 0.56 for oxygen). The rates calculated assuming the reaction to be

first order with respect to both reactants are smaller than the rates calculated using the orders determined by Chen and Morris (1972a). At very low oxygen concentrations, there is a factor of six difference in the rates, but as the oxygen concentration increases, the rates approach each other.

TABLE 16

Comparison of Calculated Sulfide Oxidation Rates
(Initial Reaction Rates)

Initial Reaction Concentration (μM)		Chen and Morris' Rate Law using their orders(1)	Chen and Morris' Rate Law assuming second order overall(2)	Cline & Richards Rate Law @10°C(3)	Cline & Richards Rate Law @25°C(4)
$[O_2]$	$[\Sigma S^{=}]$				
10	65	0.066	0.011	1.95	5.85
75	65	0.20	0.083	14.6	43.8
250	65	0.40	0.28	48.7	146
160	100	0.65	0.32	24	72
50	300	1.5	0.30	22.5	67.5
300	300	4.1	1.8	135	405
600	300	6.0	3.6	270	810

Calculations:

(1) Rate = $K[O_2]^{.56}\ [\Sigma S^{=}]^{1.34}$ where $K \simeq 20/M^{0.9}$ -hr @ pH ≃ 8 and 25°C. $[O_2]$ and $[\Sigma S^{=}]$ expressed in Molar units.

(2) Rate = $K[O_2]\ [\Sigma S^{=}]$ where $K = 20/M^{0.9}$ -hr, as above, but the rate is assumed to be first order with respect to both reactants.

(3) Rate = $K^1[O_2]\ [\Sigma S^{=}]$ where $K^1 = 1.5 \times 10^{-3}/\mu M$ -hr @ pH ≃ 7.5 to 7.8, T = 9.8°C.

(4) Calculated by assuming a factor of two increase in the rate per 10 degree rise in temperature.

Rates calculated using the expression of Cline and Richards (1969) are two orders of magnitude greater than those calculated using the expression of Chen and Morris (1972a). Cline and Richards (1969) performed their experiments in sea water, which contains, among other metal ions, approximately 50 mM magnesium and 10 mM calcium. The sea water no doubt contains trace quantities of the divalent transition metal ions which Chen and Morris (1972b) showed can greatly increase the rate of reaction even when present in micromolar concentrations. The expression of Chen and Morris (1972a) yields a lower limit to the rate. Sorokin (1970) estimated sulfide oxidation rate at the interface of oxic and anoxic waters in the Black Sea to be 0.13 μM/hr , a value that agrees well with rates calculated using Chen and Morris' expression.

Bacteria increase the rate of sulfide oxidation. However, Sorokin (1970) suggests that oxidation of aqueous sulfide in the Black Sea proceeds chemically, but that bacteria are probably important in converting the products of chemical oxidation (e.g., sulfur, thiosulfate, etc.) into sulfate.

There is evidence that the major product of chemical sulfide oxidation in sea water is elemental sulfur and/or polysulfides. Cline and Richards (1969) suspected that elemental sulfur was the major project in their experiments, Chen and Morris (1972b) found that the major product in the presence of many of the metal ions that catalyzed the reaction was elemental sulfur. Dr. J. Leckie (personal communication) found that, for the oxidation of solid ferrous sulfide in sea water by dissolved oxygen, the major product was elemental sulfur. A suite of products was observed in media with lower ionic strengths.

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APPENDIX 2
CIRCULATION

I. INTRODUCTION

Exchange of sea water in the Southern California Bight with open oceanic waters is limited by the vertical water density structure and by the benthic topography. The alternation of mountains and valleys that dominates Southern California landscape continues for up to 40 km to sea. These mountain ranges isolate waters in the valleys from each other. With horizontal movements limited by valley walls and vertical movement controlled by density stratification, each water mass develops its characteristics separated from the ocean ocean. Just as the blockage of winds by the mountains ringing the Los Angeles Basin has caused a smog problem, so have the offshore mountains caused the accumulation of low-oxygen conditions in bottom waters.

Extent to which water at a given location is isolated from the open ocean varies considerably. Surface waters can move through the bight with flow interrupted only by the mainland or the offshore islands. Barriers to water movement increase with depth, cutting off cummunication between Santa Barbara and Santa Monica Basins around 250 m depth, between Santa Cruz Basin and the open ocean at 350 m (Figure 2). Valley waters at these intermediate depths are trapped in dead end canyons, exchanging horizontally through slow turbulent processes with waters outside. Deeper, in what have been called basins, surrounding valley walls cut off waters from all horizontal communication with the open ocean.

Oxygen is a substance whose concentration is changed by biological processes. Near the surface, dissolved oxygen concentration (DO) is kept at approximately 0.25 moles m^{-3} by contact with the atmosphere. Oxygen in deeper waters is depleted by the oxidation of organic matter. Higher oxygen consumption rates in coastal waters lead to depletion of oxygen in valley waters relative to open oceanic waters (Figure 6). Resulting concentrations are determined by rates of oxygen consumption relative to rates of resupply.

Currents in the surface region of the Southern California Bight are complex, involving the California Current, the Southern California Countercurrent and wind stresses (Jones 1971). Residence time for surface water in the bight is about 3 months. The rapid turnover and high oxygen concentrations of these surface water protect them from major changes induced by sludge disposal.

Bottom water sources have been studied by following water tracers (Emery 1960). Exchange in these basins is controlled by water at the depth of the lowest gap in the surrounding valley wall. Over this gap, called the sill, flows a variable amount of denser water which sinks to the bottom, bringing more oxygen (Sholkovitz and Gieskes 1971). This flow can come in a torrent, displacing all the old basin water, or it can come in a relatively continuous trickle, causing a continuous upward flow of more than 0.1 m day^{-1}. There is also a continuous vertical eddy diffusion exchange which allows basin waters to mix with overlying waters. These two processes of vertical advection and eddy diffusion keep basin waters from total isolation.

There have been no studies on exchange rates at intermediate depths. Intermediate waters will exchange with basin waters below and surface waters above through vertical advection and eddy diffusion. They will also exchange laterally down the canyons and through the openings by way of horizontal diffusion and dispersion processes. These intermediate waters will be called upper basin waters to emphasize their isolation from rapid horizontal exchange processes characteristic of the surface layer; bottom basin waters will be called lower basin waters to distinguish them from the upper basins.

II. ONE DIMENSIONAL MODELS

Vertical profiles have been taken over a wide area in Santa Barbara Basin (Sholkovitz 1972) and in Santa Monica and San Pedro Basins (Minard 1968). Vertical distributions within a basin vary but show no apparent horizontal gradients. Horizontal variations are the result of temporary vertical movements caused by internal waves. Because horizontal gradients are smaller than vertical gradients, we have assumed that waters within a basin are horizontally well mixed, that important processes cause vertical variations and, therefore, that concentration of a substance depends only on the depth.

The concentration of a substance at a given depth can be described in terms of the various processes influencing it. The total amount in a slice dz thick, at a depth z, where the basin cross section is A(z) and the concentration C(z) is A(z)C(z)dz. Changes in this will result from vertical advection, particle settling, eddy diffusion, and various sources and sinks:

$$\frac{\partial(AC)}{\partial t} = \left.\frac{\partial(AC)}{\partial t}\right|_{\substack{\text{advection}}} + \left.\frac{\partial(AC)}{\partial t}\right|_{\substack{\text{particle}\\\text{settling}}} + \left.\frac{\partial(AC)}{\partial t}\right|_{\substack{\text{eddy}\\\text{diffusion}}} + \left.\frac{\partial(AC)}{\partial t}\right|_{\substack{\text{sources,}\\\text{sinks}}} \qquad (1)$$

Each of these terms can be mathematically described.

Vertical Advection

Concentration change for an advection process is a function of flow velocity, v_f(m d^{-1}), and concentration. Flow velocity is related to mass flow, Q($m^3 d^{-1}$); $Q = v_f A$. Upward water velocity in the basins

decreases as the cross sectional area increases, but the flow, Q, remains constant. Therefore

$$\left.\frac{\partial(AC)}{\partial t}\right|_{\text{advection}} = -\frac{\partial}{\partial z}(v_f AC)$$

$$= -\frac{\partial}{\partial z}(QC)$$

$$= -Q\frac{\partial C}{\partial z} \quad . \tag{2}$$

It has been assumed that the water flows in along the bottom of the basins, and hence this applies only above the inflow layer on the bottom. Since z is positive in the downward direction, Q for upward advection would be a negative quantity.

Particle Settling

The mathematical description of particle settling is similar to that of advection. For constant particle settling velocity, v_s (m d^{-1}),

$$\left.\frac{\partial(AC)}{\partial t}\right|_{\substack{\text{particle}\\ \text{settling}}} = -\frac{\partial}{\partial z}(v_s AC)$$

$$= -v_s A\frac{\partial C}{\partial z} - v_s C\frac{\partial A}{\partial z} \tag{3}$$

Eddy Diffusion

Communication of basin waters with adjacent waters outside the basin will be described differently than with overlying basin waters. Vertical mixing(when the vertical eddy diffusion coefficient is

$\varepsilon_z (m^2 d^{-1})$)is given by

$$\left.\frac{\partial (AC)}{\partial t}\right|_{\substack{\text{vertical}\\ \text{eddy diffusion}}} \approx \frac{\partial}{\partial z}\left(\varepsilon_z A \frac{\partial C}{\partial z}\right)$$

$$= \varepsilon_z A \frac{\partial^2 C}{\partial z^2} + \varepsilon_z \frac{\partial A}{\partial z} \frac{\partial C}{\partial z}$$

assuming $\varepsilon_z \approx$ constant.

Horizontal exchanges of this layer will depend on the concentration gradient at the openings and the width of the openings:

$$\left.\frac{\partial (AC)}{\partial t}\right|_{\substack{\text{horizontal}\\ \text{eddy diffusion}}} = W(z) \left.\varepsilon_y \frac{\partial C}{\partial y}\right|_{\text{opening}} = -W(z) K \Delta C$$

where ε_y is the horizontal eddy diffusion coefficient ($m^2\ d^{-1}$); W(z) is the width of the basin openings at z(m); ΔC = concentration inside minus concentration outside basin near the opening; and K is an exchange coefficient.

The total effect of eddy diffusion is the sum of these two processes,

$$\left.\frac{\partial (AC)}{\partial t}\right|_{\substack{\text{eddy}\\ \text{diffusion}}} = \varepsilon_z A \frac{\partial^2 C}{\partial z^2} + \varepsilon_z \frac{\partial A}{\partial z} \frac{\partial C}{\partial z} - WK\Delta C \qquad (4)$$

Sources and Sinks

Source and sink terms in the conservation equation (1) account for distributed additions or removals of a substance. One such source could be sludge discharge. For example, if B(moles d^{-1}) is the discharge rate of organic carbon, and if this carbon enters in a uniform 10 m layer, the source term g(z) (moles $m^{-1} d^{-1}$) would be B/10

at the depth of the layer and zero elsewhere. Consequently,

$$\left.\frac{\partial(AC)}{\partial t}\right|_{\text{source}} = g(z) \tag{5}$$

Sinks can be any of the various processes which remove a substance such as reaction with the bottom, radioactive decay, or chemical reactions. Reactions with the bottom will depend on the bottom area in contact with a slice. That area for a slice dz thick is $-\frac{dA}{dz}\,dz$. Thus, the loss to the volume of water dz thick at depth z caused by particle sedimentation on the bottom is

$$\frac{\partial(ACdz)}{\partial t} = -v_s C\left(-\frac{dA}{dz}\,dz\right)$$

or

$$\left.\frac{\partial(AC)}{\partial t}\right|_{\substack{\text{bottom}\\ \text{sedimentation}}} = +v_s C\,\frac{dA}{dz} \tag{6}$$

Similarly, oxygen uptake by the sediments will reduce oxygen concentrations. If $\ell(C,z)$ (moles $m^{-2}d^{-1}$) is the oxygen uptake of the sediment, then

$$\left.\frac{\partial(AC)}{\partial t}\right|_{\text{sediment}} = \ell(C,z)\,\frac{dA}{dz}\,. \tag{7}$$

For a radioactive substance, a constant fraction is always disappearing. The radioactive decay loss is

$$\left.\frac{\partial(AC)}{\partial t}\right|_{\text{decay}} = -\lambda AC \tag{8}$$

where λ is the decay rate (d^{-1}).

Chemical reaction would be represented in the same way. If $r(d^{-1})$ is the reaction rate for the appearance (or disappearance) of C, then

$$\left.\frac{\partial(AC)}{\partial t}\right|_{\text{reaction}} = rAC \tag{9}$$

The Differential Equation

The differential equation for a given substance consists of the sum of all the appropriate terms. Settling and radioactive decay are not important for oxygen, so the oxygen conservation equation would be

$$A\frac{\partial C}{\partial t} = -Q\frac{\partial C}{\partial z} + \varepsilon_z\left(A\frac{\partial^2 C}{\partial z^2} + \frac{\partial A}{\partial z}\frac{\partial C}{\partial z}\right) - WK\Delta C + \ell\frac{dA}{dz} + r\,AC$$

which becomes at steady state ($\frac{\partial C}{\partial t} = 0$):

$$0 = \frac{\partial^2 C}{\partial z^2} + \frac{\partial C}{\partial z}\left(\frac{1}{A}\frac{dA}{dz} - \frac{v_f}{\varepsilon_z}\right) - \frac{WK\Delta C}{\varepsilon_z A} + \frac{\ell}{\varepsilon_z A}\frac{dA}{dz} + \frac{rC}{\varepsilon_z} \tag{10}$$

For organic sludge particles, of concentration C, the particle settling terms are important. The equation is

$$A\frac{\partial C}{\partial t} = -Q\frac{\partial C}{\partial z} - v_s\left(A\frac{\partial C}{\partial z} + C\frac{dA}{dz}\right) + \varepsilon_z\left(A\frac{\partial^2 C}{\partial z^2} + \frac{dA}{dz}\frac{\partial C}{\partial z}\right) - WK\Delta C$$

$$+ g(z) + v_s C\frac{dA}{dz} + rAC$$

At steady state,

$$0 = -\frac{\partial^2 C}{\partial z^2} + \frac{\partial C}{\partial z}\left(\frac{1}{A}\frac{dA}{dz} - \frac{v_s}{\varepsilon_z} - \frac{v_f}{\varepsilon_z}\right) - \frac{WK\Delta C}{A\varepsilon_z} + g(z) + rAC \tag{11}$$

For temperature, T, at steady state

$$0 = \frac{\partial^2 T}{\partial z^2} + \frac{\partial T}{\partial z}\left(\frac{1}{A}\frac{dA}{dz} - \frac{v_f}{\varepsilon_z}\right) + \frac{WK\Delta T}{A\varepsilon_z}. \tag{12}$$

III. PROCESS RATES IN THE LOWER BASIN

Vertical Eddy Mixing Rates

Chung (1973) measured concentrations of excess-radon in Santa Barbara Basin and used the results to calculate the vertical eddy-diffusion there. The radioactive element radon-222 is released from the sediments as a decay product of radium-226. Excess radon, the concentration of ^{222}Rn corrected for input from decay of dissolved ^{226}Ra, depends only on mixing rate and radioactive decay rate. Excess radon profiles were fit to determine the vertical eddy mixing rate. Chung (1974) used a model that included vertical eddy mixing and radioactive decay, but not advection:

$$\varepsilon_z \frac{d^2C}{dz^2} - \lambda C = 0$$

where C is the concentration of excess radon
z is the distance above the bottom, and
λ is radon decay rate, 1.8×10^{-1} day^{-1}.

He estimated ε_z, the eddy diffusion coefficient, to be 3.9 cm^2 sec^{-1} (33.5 $m^2 day^{-1}$).

This model ignores vertical advection, shown by Sholkovitz (1972) to be important in the basin. A more complete model would also take into account the vertically varying geometry. Such a model would be:

$$\varepsilon_z\left(\frac{d^2C}{dz^2} + \frac{1}{A}\frac{dA}{dz}\frac{dC}{dz}\right) - v_f \frac{dC}{dz} - \lambda C = 0$$

or

$$\frac{d^2C}{dz^2} + \frac{dC}{dz}\left(\frac{1}{A}\frac{dA}{dz} - \frac{v_f}{\varepsilon_z}\right) - \frac{\lambda C}{\varepsilon_z} = 0 \qquad (13)$$

where v_f is the vertical velocity, and $\frac{1}{A}\frac{dA}{dz}$ may be determined from the depth-area relationship (Figure 7).

Further problems with using a one-dimensional model to calculate an eddy diffusion coefficient in Santa Barbara Basin arise because interaction of bottom topography with horizontal mixing process can either increase or decrease radionuclide concentrations: mixing with water next to basin walls will increase the concentration, mixing with water near the basin center will decrease the concentration. Thus, the mixing value calculated by Chung is only approximate.

Vertical eddy diffusion coefficient values in the open ocean are about 4 $m^2\ d^{-1}$. The values in the basins might be expected to be between 4 and 40 $m^2\ d^{-1}$. We have used 19 $m^2\ d^{-1}$ in calculations reported here. Further discussion and probable adjustment of the diffusivity value will be given in the final report.

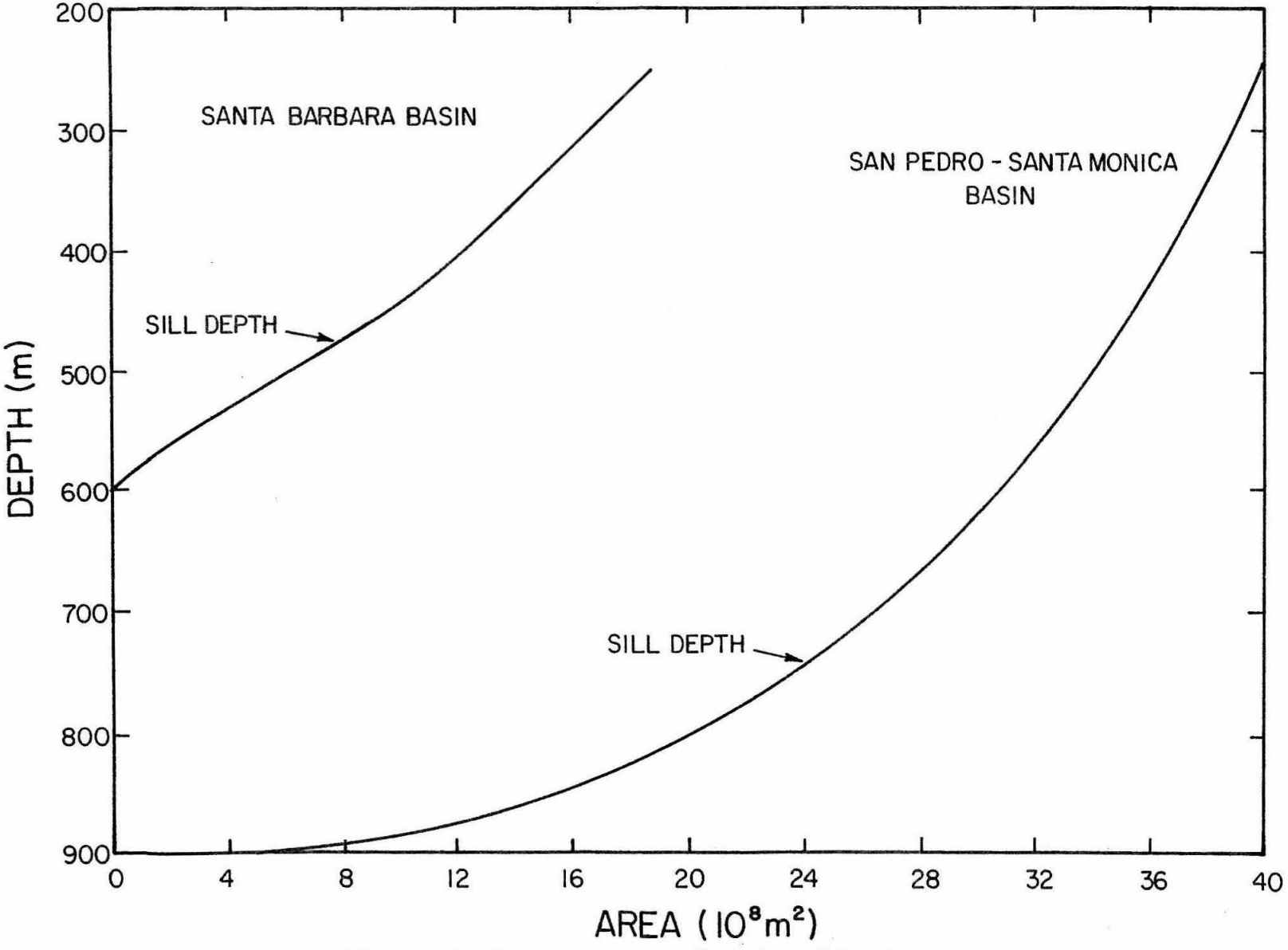

Figure 7. Basin Area as a Function of Depth

Box Model

Sholkovitz (1972) estimated rates of oxygen consumption in the lower Santa Barbara Basin by observing the decrease in oxygen after basin waters had completely flushed. He also calculated advection rates using Chung's estimate for the eddy diffusion under assumed steady state conditions. We have reestimated these rates using a lower estimate for the eddy diffusion coefficient and including non-steady state conditions.

The box model that we used considers there to be only two physical inputs into the lower basin: vertical advective flow entering at the bottom and leaving at the sill depth, and eddy diffusive exchange at the top (or sill depth). Vertical water flow is initiated by colder, denser water from outside a basin rising higher than the sill. This water, denser than the basin water, flows to the basin bottom displacing basin water upward. This upward displacement is the vertical advection. Eddy mixing brings heat and buoyancy to the new bottom water so that it, too, will be displaced upward with the next influx of outside water (Sholkowitz 1972, Emery 1960). The rate a substance is brought in by this water is the product of the flow rate and the concentration: input at bottom = $Q \cdot C(\text{input})$ where Q is the volume flow ($m^3 d^{-1}$) and C(input) is the concentration in the incoming water.

At the sill depth, which is the boundary between the upper and lower basins, material is exchanged through both eddy diffusion and net flow. Advection will carry material out at a rate equal to Q C(sill), where C(sill) is the concentration at the sill depth. Eddy mixing will carry material out at a rate equal to the flux times the surface area. Flux out is equal to the concentration gradient times the eddy diffusion coefficient. Thus, outflow at top is $QC(sill) + A\varepsilon_z \left.\frac{dC}{dz}\right|_{sill}$ with units of substance per day (z positive down).

Total amount of a substance in the basin will change with the rate determined by inflow, outflow, and any regeneration or consumption in the basin. If R is the rate of change of total amount of a substance in a basin, in units of substance day^{-1}, then

$$R = QC(in) - QC(sill) - A\varepsilon_z \left.\frac{dC}{dz}\right|_{sill} + (source) - (sink)$$

The data collected by Sholkovitz for Santa Barbara Basin on six cruises over a period of more than a year can be used to estimate R, C(in), C(sill), and $\frac{dC}{dz}$. We fit the vertical concentration data to the distribution $C = a + be^{\beta z}$ using a least-squares parameter fitting technique. The parameters, a, b, and β were used to estimate $\frac{dC}{dz}$ and to provide the concentration as a function of depth. A volume integration yielded total substance in the basin at the time of the cruise.

Flow rates were calculated using temperature data. T(in) for a given period was assumed to be the average of bottom temperatures obtained during the cruises at the beginning and at the end of that period. T(sill) and $\frac{dT}{dz}$ were estimated in the same way. The rate of change of total heat content was estimated by dividing the difference between total heat content before and after by the time period (Table 17).

The results show the flow to be $2.51 \pm 1.7 \times 10^8$ $m^3 d^{-1}$. This represents a flow velocity of 0.38 ± 0.26 m d^{-1} at the depth of the sill. The flow if the basin is assumed to be at a constant temperature (i.e. R=0) is $1.65 \pm .46 \times 10^8$ m^3 d^{-1}.

Rates of nitrate and silicate regeneration and oxygen consumption can be calculated the same way using these flow rates if the incoming concentrations are known. If water flowing in has a constant relationship with temperature, and if this relationship is the same as that in a profile taken outside of Santa Barbara Basin by Sholkovitz (Station 6 on cruise SBJULY*70) then the oxygen (or nitrate or silicate) concentration of incoming water can be calculated using the bottom temperature as a nutrient tracer. The results (Table 18) are quite consistent, although with occasional (large) anomalies. Thus, the average of all 5 rates calculated indicates silicate is being regenerated at a rate of $6.5 \pm 13 \times 10^6$ moles d^{-1}, but elimination of the unbelievable negative rate gives $12 \pm 3 \times 10^6$ moles d^{-1}. Similarly, for nitrate the rate is

Cruise Data				Rate Data				
Cruise	Basin Heat Content* (10^9 M cal)	$\nabla T\|_{sill}$ (10^{-3}° C/m)	$T_b - T_{sill}$† (°C)	Interval (days)	ΔBasin Heat (10^7Mcal/day)	$T_b - T_t$ (°C)	$\nabla T\|_{sill}$ (10^{-3}°C/m)	Q ($10^8 m^3 d^{-1}$)
NØDØC	13.1	-5.1	-.25	210	-0.71	-.16	-3.0	2.77
DEC 69	11.6	-0.8	-.09	39	-1.80	-.11	-1.2	2.97
JAN 70	10.9	-1.5	-.15	100	-5.5	-.18	-1.8	4.29
MAY 70	5.4	-2.0	-.20	31	+3.5	-.21	-2.2	-0.4
JUN 70	6.5	-2.4	-.22	30	-1.3	-.19	-3.2	2.84
JUL 70	6.1	-4.0	-.16					

* ΔT of 1°C assumed equal to 1 Megacalorie m^{-3}. Heat content expressed relative to heat content at 6.22°C.

† T_b is temperature at basin bottom.

TABLE 17

Vertical advection calculations for lower Santa Barbara Basin using data of Sholkovitz (1972). $Q = (\Delta\text{Basin heat} + \varepsilon_z A \frac{dT}{dz}|_{sill})/(T_b - T_t)$, $\varepsilon_z = 19\ m^2 d^{-1}$. $Q = 2.5 \pm 1.7 \times 10^8\ m^3\ d^{-1}$ with negative value, $3.2 \pm .7 \times 10^8\ m^3\ d^{-1}$ without. If ΔBasin heat is assumed equal to 0, $Q = 1.65 \pm .46 \times 10^8\ m^3\ d^{-1}$. $A(sill) = 6.6 \times 10^8\ m^2$, volume of lower basin $= 4.3 \times 10^{10}\ m^3$.

Cruise	Interval (d)	Flow Rates: Flow(Q) ($10^8 m^3 d^{-1}$)	Flow Rates: v_f(sill) ($m d^{-1}$)	Sources: Silicate (10^6 moles d^{-1})	Sources: Nitrate (10^6 moles d^{-1})	Sink: Oxygen (10^6 moles d^{-1})
NØDØC	210	2.77	0.42	11.6	-3.2	7.5
DEC 69	39	2.97	0.45	9.7	1.2	11.6
JAN 70	100	4.29	0.65	10.8	1.8	-3.0
MAY 70	31	-0.4	-0.06	-16	2.3	4.8
JUN 70	30	2.84	0.42	16.4	3.2	2.1
JUL 70						
MEAN ± SD				6.5 ± 13	1.1 ± 2.5	4.6 ± 5.5
MEAN ± SE				6.5 ± 5.8	1.1 ± 1.1	4.6 ± 2.5
without odd signed value, mean ± SD				12 ± 3	2.1 ± .8	6.5 ± 4

TABLE 18

Process rates in lower Santa Barbara Basin. Sources are regenerated in the basin, sinks consumed.

$1.1 \pm 2.5 \times 10^6$ moles d^{-1}, with all of the values and $2.1 \pm 0.8 \times 10^6$ moles d^{-1} without the negative value; for oxygen the consumption rate is $4.6 \pm 5.5 \times 10^6$ moles d^{-1}. The variation in these rates might better be represented by the standard error rather than the standard deviation because, presumably, the regeneration or consumption processes are fairly constant. The standard error for five measurements is 0.44 times the standard deviation.

These estimates for flow through Santa Barbara Basin are quite close to those made by Sholkovitz (1972). His estimate for flow rate was $2.6 - 4.3 \times 10^8$ m^3 d^{-1} and for oxygen consumption was $5.2\text{-}7.6 \times 10^6$ mole d^{-1}.

We did not have consistent series of measurements for lower San Pedro and Santa Monica Basins as we did for Santa Barbara Basins. We computed water flow and oxygen consumption rates assuming that the basins were at steady state. Sholkovitz (1972) suggested that this is the case, because these basins have historically been more thermally constant than Santa Barbara Basin. Detailed temperature and oxygen profiles made by Minard in 1968, Sholkowitz in 1970 and by the Bureau of Land Management in 1976 all show remarkably similar temperatures and oxygen concentrations (Table 19). The flow rate estimate for the joint San Pedro-Santa Monica Basin is $5.57 \pm 2.6 \times 10^8$ m^3 d^{-1}. Oxygen consumption rate estimate for the lower basin is $7.6 \pm 6.7 \times 10^6$ moles d^{-1}.

The relatively higher error in oxygen consumption rate is probably due to the uncertainty in oxygen content in the incoming water. Oxygen concentration in basins around San Pedro-Santa Monica Basin at the temperature of 5.05°C averaged 0.34 ± 0.10 liter m^{-3}. The highest and the

Cruise	T_{bott} (°C)	DO_{sill} ($\ell\ m^{-3}$)	flow(Q) ($10^8 m^3 d^{-1}$)	v_s - sill ($m\ d^{-1}$)	$DO_{consump}$ (10^6 mole d^{-1})
OPBASIN (Sholkovitz 1972)	5.04	0.22	7.6	0.31	5.8
BLM (S.A.I.)	5.03	0.22	2.7	0.11	1.9
FWPCA (Minard 1968)	5.08	0.22	6.4	0.26	15.4
Mean ± SD			5.7 ± 2.6	.22 ± .10	7.6 ± 6.7

TABLE 19

Rates in lower Santa Monica-San Pedro Basin under assumed steady-state conditions. Oxygen concentration at 5.05°C found in other basins was 0.34 ± 0.10 ℓ/m^3. Therefore, $(DO_{B_2} - DO_T)$ was 0.12 ± 0.10 ℓ/m^3. Lower basin area at sill depth is $2.46 \times 10^9\ m^2$.

lowest concentrations were both measured in the same area, Santa Cruz Basin. Differences in incoming oxygen concentration can seriously affect the estimate of oxygen consumption rates.

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APPENDIX 3

SCOPE OF WORK (From EQL-LA/OMA Contract, August 24, 1977)

Objective of this study is to explore environmental effects of variations of existing ocean disposal practices for digested sewage sludge resulting from:

(a) full secondary treatment and
(b) marine secondary treatment

SCOPE OF WORK

A. The purpose of LA/OMA Task 5.2 is to assess the environmental effects of variations in present methods for ocean disposal of treated sewage sludge. The presence of low oxygen basins not far offshore is a feature of the Southern California Bight which should be explored as a possible sludge disposal site. With regard to the low oxygen basins, particular questions to be investigated include:

1. Mechanisms and rates of water exchange between oceanic and basin waters.
2. Present rates of oxygen supply and utilization in low oxygen basins.
3. Chemical and geological composition of basin floors.
4. Comparison of natural organic deposition rate with that of sewage solids.
5. Fate of sludge particles discharged in ocean basins.
6. Projected oxygen, sulfide and selected trace metal concentrations upon addition of sewage sludge.
7. Fate of oxygen deficiency, sulfides and trace metals in water discharged from basins.
8. Effects of sludge discharge on benthic and planktonic animals, both in the basins and in surrounding waters.

B. Similar questions should be posed and answered about the effect of extending sludge discharge into waters of various depths greater than 100 m (present depth of Hyperion discharge) up to 900 m in the deep basins. A comparison will be made of the predicted effects of discharge at various depths.

C. Only a small amount of field work (to be a separate contract by SCCWRP) is anticipated at this stage of investigation because of limited time and funds. The most urgent need is for current data which is non-existent in the literature; however, some additional biological work will also be undertaken by SCCWRP. As part of this task a program of needed additional pre-design field studies will be delineated if this system appears feasible. Determination of the feasibility will be determined jointly by LA/OMA Project and EQL.

D. The Report of findings will include a discussion and evaluation of risks and uncertainties.

TIME SCHEDULE AND REPORTS

A one-year period is required, with submittal of an interim progress report by December 20, 1977, and a final report by June 30, 1978.

CORRDINATION WITH SCCWRP

Since the results of field work by SCCWRP will be needed as soon as possible, arrangements will be made for transfer of SCCWRP data to this project just as soon as each segment of data becomes available. SCCWRP's final data report will be in final report of the Environmental Quality Laboratory of the INSTITUTE (EQL) as an appendix. (It will be SCCWRP's responsibility to provide to EQL reproducible masters ready for printing.)

Furthermore, EQL's interim report will be sent to SCCWRP (as well as other agencies) for review and comment. All suggestions will be carefully considered, and any revisions will be made on the final report at the discretion of the EQL principal investigators. EQL will provide LA/OMA Project with copies of the comments and suggestions received.

KEY PERSONNEL

Key personnel to be assigned to the contract and the estimated allocation of revenues are shown in Table 1.